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PHOTO-ELECTRICITY

THE LIBERATION OF ELECTRONS
BY LIGHT

WITH CHAPTERS ON FLUORESCENCE &
PHOSPHORESCENCE, AND PHOTO-
CHEMICAL ACTIONS &
PHOTOGRAPHY

BY

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PREFACE

THE present book is based on a course of advanced lectures delivered by the author at King's College, London, during the Lent Term of 1910; but the greater part has been entirely rewritten so as to incorporate the results of the large amount of research carried out in the three years since these lectures were given.

The only account of the subject of photo-electricity that has so far been published in the English language is that contained in Sir J. J. Thomson's book, *The Conduction of Electricity through Gases* (Second Edition, 1906). A summary of later work, up to the year 1909, has been published by R. Ladenburg in German in an article of 60 pages in the *Jahrbuch der Radio-aktivität*. Since this appeared no detailed survey of the whole subject has been attempted. Although many interesting questions still await investigation, the work done during the last few years has settled the foundations of the subject on a firm basis, and therefore the present appears a favourable time to give a connected account of what has been accomplished.

Starting from the observation of Hertz in 1887 that the incidence of ultra-violet light facilitated the passage of an electric spark, and from the discovery of Hallwachs, immediately following, that a negatively charged body readily lost its charge when illuminated by ultra-violet light, the subject reached its culminating point in the identification and measurement of the natural unit of negative electricity, the electron or corpuscle, by Sir J. J. Thomson in 1899. Thus photo-electric action, from the point of view of our present theories, is the separation or liberation of negative electrons from matter under the influence of radiation, generally of short wave-length. It remains then to determine how the

velocity and the number of the electrons emitted depend upon the conditions of the experiment, and if possible to form some conception of the mechanism of the process by which the incidence of electro-magnetic waves results in the emission of electrons. Thus our subject is connected, in the most intimate fashion, with one of the outstanding questions of modern physics—the nature of radiation. It may well be that further study of photo-electric phenomena will serve to reconcile the quantum or unitary theory of radiation with the accepted undulatory theory of light. Some progress at least in this direction has been made already, and it would appear probable that the emission of energy in radiation is discontinuous because the emission of electrons is discontinuous.

It will be seen from the introductory chapter, which gives an outline of the whole, not only that the subject is of great theoretical interest, but also that it is connected with questions of great practical importance through its relation to photo-chemical processes of all kinds. In the later chapters the subject is developed in greater detail, with due regard to the historical setting of each investigation. Special attention may perhaps be directed to the chapters dealing with the influence of the character of the light on photo-electric phenomena, and with the theories of photo-electric action. The chapter on photo-electric fatigue deals with a part of the subject which I have myself specially investigated. In discussing fluorescence and phosphorescence I have given an account of the theories of Stark and of Lenard, which have not as yet been described in any English text-book. In the last chapter I have considered the bearing of the facts of photo-electricity on photo-chemical processes in general and photographic changes in particular, and I have endeavoured to develop the view taken by Professor Joly as to the nature of the latent photographic image, and have attempted an explanation of the complicated phenomena of photographic reversal.

In connection with the diagrams illustrating the text I am indebted to the Royal Society of London, the Royal Society of Edinburgh, the Royal Photographic Society,

Messrs. Taylor & Francis, the publishers of the *Philosophical Magazine*, Messrs. S. Hirzel of Leipsic, and Messrs. Vieweg & Son of Brunswick.

In conclusion, I wish to thank all those whose assistance has made possible the writing of this book, and in particular I must mention Professor Wilhelm Hallwachs, Dr. Rudolf Ladenburg (in connection both with his own work and with that of his brother, Dr. Eric Ladenburg, whose early death is regretted by all workers in this subject), Dr. Robert Pohl, Professor O. W. Richardson, Dr. J. Robinson, and Dr. W. M. Varley. I must also thank my colleague Mr. G. H. Martyn for help in the preparation of the manuscript, Mr. Stanley Maxwell for reading the proof sheets, and finally the Editors of the Series for the very valuable suggestions and advice which they have given me during the completion of the work.

H. STANLEY ALLEN.

UNIVERSITY OF LONDON,
KING'S COLLEGE,
September 1911.

CONTENTS

CHAP.	PAGE
I. INTRODUCTORY	I
II. THE EARLY EXPERIMENTERS	13
III. THE EMISSION OF NEGATIVE ELECTRONS IN A VACUUM	22
IV. THE VELOCITY OF THE ELECTRONS	35
V. THE PHOTO-ELECTRIC CURRENT IN GASES AT VARIOUS PRESSURES	49
VI. PHOTO-ELECTRIC SUBSTANCES: SOLIDS AND LIQUIDS	68
VII. PHOTO-ELECTRIC SUBSTANCES: GASES AND VAPOURS	88
VIII. THE INFLUENCE OF TEMPERATURE ON THE PHOTO-ELECTRIC DISCHARGE	96
IX. THE INFLUENCE OF THE CHARACTER OF THE LIGHT ON THE PHOTO-ELECTRIC DISCHARGE: SOURCES OF LIGHT, INFLUENCE OF THE INTENSITY OF THE LIGHT	106
X. THE INFLUENCE OF THE CHARACTER OF THE LIGHT ON THE PHOTO-ELECTRIC DISCHARGE (<i>continued</i>): IN- FLUENCE OF THE PLANE OF POLARISATION AND OF THE WAVE-LENGTH OF THE LIGHT	118
XI. THEORIES OF PHOTO-ELECTRIC ACTION	142
XII. PHOTO-ELECTRIC FATIGUE	159
XIII. FLUORESCENCE AND PHOSPHORESCENCE	180
XIV. PHOTO-CHEMICAL ACTIONS AND PHOTOGRAPHY	198
INDEX OF AUTHORS	217
INDEX OF SUBJECTS	220

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(Photo-electric Fatigue.)

CHAPTER I

INTRODUCTORY

THE term Photo-electricity is used in a general sense to designate any electrical effect due to the influence of light. Thus the change of electrical resistance of selenium, when exposed to light, is spoken of as a photo-electric action. In this book the term is used in a more restricted sense, to denote a change in the state of electrification of a body produced by the action of light. Since ultra-violet radiation is most effective in bringing about such changes, the term Actino-electricity is sometimes used.

In accordance with modern electrical theory we regard light as an electro-magnetic disturbance, and a change in electrification as due to the addition or removal of negative electrons. From this standpoint, a photo-electric change is equivalent to the liberation of negative electrons under the influence of electro-magnetic waves. Such a process is of fundamental importance, not only in those cases where a change of electrification is readily detected, but also in connection with many other phenomena where the observed effect is of a secondary character. Amongst these we may include the change in the electrical resistance of a body due to illumination, fluorescence and phosphorescence, and all photo-chemical transformations.

The first observation in connection with photo-electricity was made in 1887 by Hertz,* who noticed that, when ultra-violet light fell upon a spark-gap, the electric discharge took place more easily than when the gap was not illuminated. The source of light might be a discharge across a second spark-gap, an ordinary flame, or an electric arc. The greater the

* Hertz, *Wiedemann's Ann. d. Physik.* 31. p. 383, 1887.

actinic quality of the source of light employed, the more powerful the effect.

In the following year Wiedemann and Ebert* showed that the action has its seat at the kathode, or negative terminal of the spark-gap.

In the same year, 1888, Hallwachs† made the important discovery that a body carrying a charge of negative electricity readily loses that charge when ultra-violet light falls upon it; on the other hand, if the body is positively charged, it is not discharged under the influence of light. This is generally referred to as the Hallwachs effect; its great significance lies in the fact that there is here a difference between positive and negative electrification—a difference that has played its part in the development of the electron theory. A little later Hallwachs and Righi showed, independently, that a body carefully insulated, and at the outset free from charge, would acquire a positive charge if exposed to ultra-violet light. The experiments referred to were carried out with brightly polished metal plates.

The experimental methods for studying the photo-electric discharge were developed by Hoor, Righi, and Stoletow. If an electric field is applied by making the illuminated metal form one plate of an air condenser, the second plate of which is charged positively by a battery, the continuous current produced can be measured by a quadrant electrometer or a sensitive galvanometer. By applying a sufficient potential difference the current becomes approximately independent of the electric field, and this “saturation” current may be regarded as a measure of the photo-electric activity of the metal.

The experiments of Elster and Geitel‡ in 1889 showed that electropositive bodies, like sodium and potassium, manifest photo-electric activity when exposed to ordinary light. Rubidium, which is still more electropositive, loses a negative charge when illuminated by the light from a glass rod which

* Wiedemann and Ebert, *Ann. d. Physik*, **33**, p. 241, 1888.

† Hallwachs, *Ann. d. Physik*, **33**, pp. 301–312, 1888.

‡ Elster and Geitel, *Ann. d. Physik*, **38**, pp. 40, 497, 1889.

is just heated to redness. Less electropositive metals show smaller activity, yet even metals such as zinc and aluminium exhibit the photo-electric effect when exposed to sunlight; but this is only the case when the surfaces are freshly polished. If the plates are allowed to stand in air, their activity rapidly diminishes. This is known as the "fatigue" of the Hallwachs effect.

As in so many other instances, the scientific study of an obscure phenomenon has resulted in an unforeseen practical return. Hallwachs* found that a plate coated with copper oxide (CuO), preserved in a small air-tight chamber, showed a photo-electric activity that was constant over long periods of time. On this he based a method of photo-electric photometry, in which the intensity of the radiation was measured by the saturation current through a photo-electric cell containing copper oxide as the substance sensitive to light. This method was used by R. Lindemann† in an investigation of the radiation from an arc lamp. Elster and Geitel,‡ who had already suggested the use of a zinc sphere for the photometry of ultra-violet light, have described a photo-electric cell designed for the measurement of the intensity of sunlight or daylight. In this case the sensitive surface is of potassium, placed in an atmosphere of argon or helium to secure permanence. The instrument resembles a small gun, and is mounted like a theodolite. It has been employed by Dember§ in a determination of the number of molecules in one gram molecule of a gas by observations on the absorption of sunlight in the atmosphere. Other photo-electric photometers have been constructed by Bergwitz|| and by Raymond¶ for the measurement of solar radiation. This method of photometry has scarcely met with the recognition which it deserves on account of its convenience and simplicity.

* Hallwachs, *Phys. Zeit.*, **5**, p. 489, 1904.

† Lindemann, *Ann. d. Physik*, **19**, pp. 807-840, 1906.

‡ Elster and Geitel, *Phys. Zeit.*, **12**, pp. 609-614, 1911; **13**, pp. 739-744, 1912.

§ Dember, *Gesell. Wiss. Leipzig. Ber.*, pp. 259-265, Nov. 1912.

|| Bergwitz, *Phys. Zeit.*, **12**, pp. 1111-1112, 1911.

¶ Raymond, *C. R.*, **154**, pp. 45-47, 1912.

In 1890 Elster and Geitel* discovered the important fact that the application of a transverse magnetic field diminished the photo-electric current, when the experiments were carried out in a gas at low pressure. This observation served to provide the method by which J. J. Thomson (1899)† and a little later Lenard,‡ and Merritt and Stewart,§ proved that the carriers of negative electricity, when a metal plate is illuminated in a good vacuum, are identical with the kathode rays of a Crookes' tube, and consist of negatively electrified "corpuscles," or negative electrons. These electrons have a mass of the order of $1/1700$ of the mass of the hydrogen atom, and carry a charge which is equal to the elementary charge in electrolytic convection.

In the photo-electric discharge at ordinary pressures, the electrons liberated at the illuminated plate form ions by becoming attached to one or more gaseous molecules, and these carriers move slowly through the gas under the influence of the electric field. If the strength of the field is greatly increased, ionisation by collision takes place, at first due to the motion of the negative electrons, but in later stages due to the motion of both positive and negative ions, until at length the discharge passes in the form of a spark.

In opposition to most other experimenters, Branly|| came to the conclusion that, in certain circumstances, positive electricity was discharged from an illuminated plate. Thus, if a piece of zinc were irradiated by the light from the sparks of a large induction coil placed sufficiently near to it, he found the loss of charge nearly as rapid for a positive as for a negative charge. Experiments by Elster and Geitel¶ have shown that the loss observed in such cases is due to the dissipation of the negative charge induced on neighbouring bodies, which are

* Elster and Geitel, *Ann. d. Physik*, **41**, p. 161, 1890.

† J. J. Thomson, *Phil. Mag.*, **48**, pp. 547-567, 1899.

‡ Lenard, *Ann. d. Physik*, **2**, pp. 359-375, 1900.

§ Merritt and Stewart, *Physical Review*, **11**, pp. 230-250, 1900.

|| Branly, *C. R.*, **110**, pp. 751, 898, 1891; **114**, p. 68, 1892; **116**, p. 741, 1893.

¶ Elster and Geitel, *Ann. d. Physik*, **57**, p. 23, 1896.

illuminated by light from the spark either directly or after reflection from the plate under test. The negative ions so produced move up to the illuminated plate under the influence of the electric field, and neutralise the positive charge. Le Bon,* also, proved that a positively electrified body could be discharged by illuminating a metal plate in its neighbourhood.

Recent experiments by Dember † in the highest attainable vacuum indicate that positively charged particles are expelled, in small numbers, from an illuminated metal plate. These are similar in their behaviour to the "canal rays" in a vacuum tube, and are probably metal atoms from which a negative electron has been liberated. It seems probable on theoretical grounds that such an action should take place, though it would only be possible for the atom to leave the solid under specially favourable conditions. Such an action would explain the alteration in the appearance of the surface after prolonged illumination, observed by Lenard, ‡ Ladenburg, § and others, and often described as a roughening of the polished surface.

Within the last decade great progress has been made in the study of photo-electric phenomena by carrying out experiments in a high vacuum, where the conditions are much simplified through the absence of a surrounding atmosphere. Two principal methods of experiment may be employed: the plate to be illuminated may be connected to an electroscope or electrometer and the positive potential which it acquires under the influence of the light measured, while surrounding bodies are kept at the potential of the earth; or the current flowing between the illuminated plate and a parallel plate may be measured by a galvanometer or electrometer, when a known difference of potential is maintained between the two plates. The first method gives information as to the maximum velocity of the electrons leaving the illuminated plate; for the positive potential rises till it attains a value sufficiently great to prevent

* Le Bon, *C. R.*, **124**, p. 755, 1897; **130**, p. 894, 1900; **135**, pp. 32-36, 1902.

† Dember, *Ann. d. Phys.*, **30**, pp. 137-165, 1909.

‡ Lenard, *Ann. d. Phys.*, **12**, p. 490, 1903.

§ Ladenburg, *Ann. d. Phys.*, **12**, pp. 558-578, 1903.

the most rapidly moving electrons from escaping. The second method measures the number of electrons leaving the illuminated surface; and, by varying the potential difference applied, it is possible to find how the number depends on the strength of the electric field. If the field is such as to retard the motion of the electrons away from the plate, only those whose velocity is sufficiently great will be able to escape; if, on the other hand, an accelerating field is applied, the number leaving the plate will rise to a maximum value, so that for further increases in the potential the current becomes approximately constant. By plotting the current against the potential, a "velocity distribution" curve is obtained, from which the proportion of electrons leaving the plate with any assigned velocity can be deduced.

A scientific study of photo-electric processes must be based on measurements of the number and velocity of the liberated electrons for varying experimental conditions.

We consider first (Chapter VIII) the influence of temperature. The early experimenters all worked at atmospheric pressure, where the results are complicated and difficult to disentangle. Experiments carried out in a good vacuum by Varley and Unwin, Lienhop, Dember, Millikan and Winchester, and Ladenburg, prove that, apart from secondary actions, both the number of electrons emitted and their velocity of emission are independent of temperature. This result holds from the low temperature secured by the use of liquid air up to temperatures at which a discharge takes place without illuminating the plate (800° C. in Ladenburg's experiments).

We turn next (Chapters IX and X) to the variations in photo-electric action produced by altering the character of the light falling upon the plate.

Experiments in a vacuum, in which the intensity of the incident light was varied, led to the two important conclusions that (1) the velocity of the electrons is independent of the intensity of the light, and (2) the number of electrons emitted is directly proportional to the intensity of the light.

The first result is due to Lenard; it has been confirmed by the experiments of Millikan and Winchester, Ladenburg,

Mohlin, Elster and Geitel, and J. R. Wright. Though the positive potential finally reached by the illuminated plate is independent of the intensity, the time taken to reach that potential increases as the intensity of the light diminishes.

The second result has received confirmation in the work of many experimenters, including Elster and Geitel, Lenard, Ladenburg, Herrmann and Richtmyer, and holds good over an extremely wide range of light intensities. There is no indication of a limiting value below which the light is inactive. For very intense sources, however, it is possible that the number of electrons emitted falls short of that required by the law of proportionality.

Elster and Geitel* in 1894 made the remarkable discovery that, in certain cases, the photo-electric effect depends upon the orientation of the plane of polarisation of the incident light. Using the liquid alloy of sodium and potassium, and allowing polarised white light to fall upon the surface at an angle of 45° , they found a maximum current when the electric vector in the light-wave was vibrating in the plane of incidence, and a minimum current when the electric vector was perpendicular to the plane of incidence.

In discussing results of this kind, it is most convenient to consider the strength of the photo-electric current in relation to the amount of light absorbed by the surface in the case under consideration. The complete discussion involves, as we shall see presently, a distinction between two actions which have been termed the "selective" and the "normal" photo-electric effect, but we may give a general explanation of the influence of the plane of polarisation in the following way. If the incident light is polarised at right angles to the plane of incidence, the electric vector in the light-wave has a component perpendicular to the surface on which the light falls. Consequently some of the electrons on which the light acts will be more likely to move in a direction at right angles to the surface, and escape from it without coming into collision with molecules of the metal. On the other hand, if the light

* Elster and Geitel, *Wied. Ann.*, **52**, p. 433, 1894; **55**, p. 684, 1895; **61**, p. 445, 1897.

is polarised in the plane of incidence, the electric vector is parallel to the surface, and the electrons will tend to move parallel to the surface. They will therefore be more likely to collide with surrounding molecules and will have less chance of escaping from the surface.

The orientation of the plane of polarisation appears to have little or no effect on the maximum velocity of emission of the electrons.*

Questions of very great interest arise in connection with the relation of photo-electric phenomena to the wave-length of the exciting light. Much attention has been paid recently to this part of the subject, and the results obtained are of great significance in considering the theory of the emission of photo-electrons.

We deal first with the variation of the photo-electric activity, as measured by the saturation current, with the wave-length of the incident light. The experiments of Elster and Geitel with the alkali metals indicate a maximum photo-electric effect for light belonging to the visible part of the spectrum. On the other hand, quantitative measurements of the specific photo-electric activity, that is, the activity for unit light intensity,† for metals tested with ultra-violet light, show an effect that increases as the wave-length diminishes. The apparent discrepancy has been explained through the work of Pohl and Pringsheim. If the electric vector of the light-wave is perpendicular to the plane of incidence, the specific photo-electric activity increases continuously as the wave-length diminishes; but if the electric vector is parallel to the plane of incidence, it becomes necessary to distinguish between two different cases. For substances which show only a "normal" photo-effect the specific photo-electric activity increases continuously as the wave-length diminishes, but the rate of increase is more rapid than when the electric vector is perpendicular to the plane of incidence. For substances which show a "selective" photo-effect the specific photo-electric activity rises to a maximum value for a particular

* Elster and Geitel, *Phys. Zeit.*, 10, pp. 457-465, 1909.

† Generally estimated in terms of the light *incident* on the surface.

wave-length (the critical wave-length), usually in the visible part of the spectrum. For very short wave-lengths these substances behave in the same way as those which show only a normal effect. The selective effect is attributed by Pohl and Pringsheim to a resonance phenomenon, but it should be remarked that the wave-lengths that are effective in producing the selective emission extend over a very wide region in the spectrum. Pohl and Pringsheim* have, however, recently shown that the maximum is much more strongly marked if the energy of the light absorbed is considered, instead of the energy of the light which is incident on the surface.

The latest experiments of Compton and Richardson† indicate that the "normal" photo-electric effect reaches a maximum similar to that reached by the "selective" effect, but farther out in the ultra-violet region of the spectrum.

A large amount of work has been carried out to determine the relation between the velocity of emission of the photo-electrons and the wave-length of the light. Recent investigations of Richardson and Compton, and of Hughes, prove conclusively that the maximum energy of emission is a linear function of the frequency of the light. For a particular metal a certain minimum frequency is necessary to produce any liberation of electrons at all. As the frequency increases, so does the energy of emission, or the positive potential required to prevent the emission.

A remarkable instance of extrapolation is afforded by the employment of the formula deduced from experiments on ultra-violet light to calculate the wave-length of Röntgen radiation, assuming this to behave in the same way as ultra-violet light of extremely short wave-length. The value so calculated (between 1 and 2×10^{-9} cm.) is in good agreement with that obtained from observations on the interference fringes produced by reflecting the radiation from a crystal of rock-salt.‡

* Pohl and Pringsheim, *Verh. Deutsch. Phys. Gesell.*, **15**, pp. 173-185, 1913.

† Compton and Richardson, *Phil. Mag.*, **26**, pp. 549-567, 1913.

‡ Barkla and Martyn, *Proc. Phys. Soc.*, **25**, p. 214, 1913.

So far we have been considering the experimental facts mainly from the historical point of view. Chapter XI is more speculative in character, being concerned with the theories that have been put forward to account for the emission of electrons from atoms of matter subject to the influence of a light-wave.

Problems of very great interest are met with in connection with the mechanism of the liberation of photo-electrons. Though recent investigations have thrown some light on these problems, many questions still remain to be answered. Photo-electric activity certainly implies the absorption of energy from the incident light; but we have to determine whether the greater part of the energy of a liberated electron is derived directly from the light, or whether the velocity of emission is practically that which the electron previously possessed in its motion within the atom, while the light merely supplies the overplus of energy required to set the electron free. The former view gives an explanation of many of the facts of photo-electricity, provided we make a special assumption as to the nature of light, and suppose that the energy of light, instead of being distributed uniformly over the wave-front, is concentrated in particular regions, so that we may think of bundles or units of light-energy. Such a "unitary theory" of light, however, does not appear to be in accordance with the electro-magnetic equations formulated by Clerk Maxwell, and unless it be possible to enunciate a theory of light which shall combine the advantages of the unitary theory with those of the well-tried undulatory theory, the assumption of a "quantum" of radiant energy has to be introduced merely to explain particular classes of facts—a proceeding not altogether desirable. Many physicists prefer to adopt the second view, that the light acts through resonance, the energy of the orbital motion of the electron being gradually increased by sympathetic light-vibrations till the electron is able to escape from the control of the forces binding it to the atom. There is additional reason to suppose that this is the correct view to take of the "selective" photo-effect, inasmuch as Lindemann *

* Lindemann, *Deutsch. Phys. Gesell., Verh.*, 18, pp. 482-488, 1911.

has calculated on fairly simple assumptions the frequency of the vibration which should correspond to maximum action. It is less clear that the view affords a sufficient explanation of the "normal" effect, seeing that we have then to assume the presence in connection with the atom of electrons with all possible frequencies of vibration, the kinetic energy being proportional to the frequency. J. J. Thomson* has suggested a theory of radiation which overcomes some of the difficulties of this view.

Another question of importance is that of the classification of the photo-electrons. We can adduce evidence which would lead us to assign the electron of the "selective" effect to the class of the valency electrons, but whether the electron of the "normal" effect belongs to the same class is far more doubtful.

In the later chapters of this book some phenomena are considered in which the liberation of electrons by light plays a fundamental part. The fascinating problem of luminescence is intimately connected with photo-electric activity, and, according to H. A. Lorentz,† the only radiation problem which can be considered as satisfactorily solved is that of phosphorescence as accounted for by Lenard.‡ The incident light effects the separation of the electron from the parent atom, and the subsequent phosphorescence is due to vibrations set up on the return of the electron. Many phosphorescent substances are good insulators, which acquire local positive charges through the liberation of photo-electrons.

Our knowledge of photo-chemical changes is not at present sufficiently great to enable us to trace all the steps of the processes involved in such changes, but the first step is undoubtedly an action on the valency electrons (chemical bonds) of the kind we have been considering. The scientific photographer may be interested in the attempt to restate the physical theory of the latent image of the photographic plate in terms of the electron theory. In this attempt I have taken Lenard's

* J. J. Thomson, *Phil. Mag.*, **14**, pp. 215-231, 1907.

† H. A. Lorentz, *Phys. Zeit.*, **11**, pp. 1234-1257, 1910.

‡ Lenard and Saeland, *Ann. d. Physik*, **28**, pp. 476-502, 1909.

theory of phosphorescence as a guide. Whatever may be the ultimate decision with regard to the debated question of a chemical change following the physical one in the formation of the latent image, the view here put forward is capable of accounting for many of the facts of photographic reversal and fulfils at least one of the functions of a theory in suggesting lines for further research.

CHAPTER II

THE EARLY EXPERIMENTERS

IN the course of his experiments on rapid electric oscillations Hertz was struck by "a noteworthy reciprocal action between simultaneous electrical sparks." These experiments have become classical, for they have given us the means of establishing that view of electrical and magnetic actions which was put forward by Faraday and developed by Clerk Maxwell, and they have found their practical application in wireless telegraphy and telephony.

In these investigations one spark, the spark A, was the discharge spark of the induction coil, and it served to excite the primary oscillation. The second, the spark B, belonged to the induced or secondary oscillation, and the length of this spark was used to measure the action set up in the secondary circuit. To facilitate the measurement, this spark was occasionally enclosed in a dark case, and it was noticed that the maximum spark length was decidedly smaller inside the case. It was found that the only portion of the case producing this effect was that which screened the spark B from the spark A.

The nature of this phenomenon was investigated by Hertz in a paper* which forms a good example of scientific method. The English translation may be found in Hertz's *Electric Waves* (pp. 63-79, 1900).

He first proved that the box did not play the rôle of an electrostatic or electro-magnetic screen. It was then shown that the ultra-violet light from the primary spark was the cause of the phenomenon, so that the paper bears the title "On an effect of ultra-violet light upon the electric discharge." "For some time, indeed," writes

* Hertz, *Sitzungsberichte d. Berl. Akad. d. Wiss.*, June 9, 1887; *Wiedemann's Ann.*, **31**, p. 383.

Hertz, "I was in doubt whether I had not before me an altogether new form of electrical action-at-a-distance. The supposition that the action was due to light seemed to be excluded by the fact that glass plates cut it off ; and, naturally, it was some time before I came to experiment with plates of rock-crystal. As soon as I knew for certain that I was only dealing with an effect of ultra-violet light, I put aside this investigation so as to direct my attention once more to the main question " (of electro-magnetic oscillations).

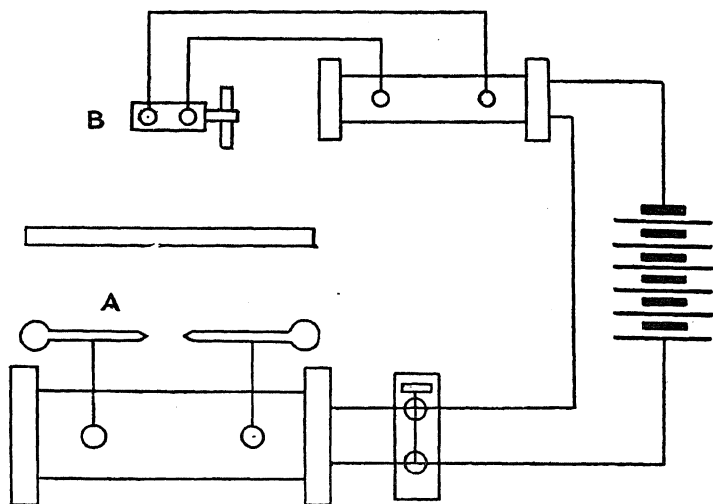


FIG. 1

It was found that the phenomena could conveniently be investigated by inserting in the same circuit the primaries of two induction coils with a common interruptor. One coil gave the spark A, usually about 1 cm. long, the other, the smaller coil, gave the spark B, usually about 1 mm. long, between the nickel-plated knobs of a spark micrometer (Fig. 1).

The apparatus was set up with the two spark-gaps parallel to one another, and when the interruptor was at work, the spark-micrometer was drawn out just as far as to allow sparks still to pass regularly.

If a plate of metal or glass was introduced between the two spark-gaps, the spark at B at once ceased ; when the plate was

removed, the spark reappeared.* The intensity of the action increased as the distance between the two sparks was diminished. The effect could be detected when the distance was 3 metres, and was easily observed at $1\frac{1}{2}$ metres. Under certain conditions the sparking distance was doubled by removing the plate. Thus the spark A exerts a certain action which tends to increase the spark length at B. A may be called the active spark, B the passive spark.

The action of the active spark does not depend on the material or the form of the poles. On the other hand, the susceptibility of the passive spark depends on its form, being greatest between knobs, least between points. There is no perceptible difference due to the metal of the terminals, but "the poles must be clean and smooth; if they are dirty, or corroded by long use, the effect is not produced."

The effect of the active spark is propagated in straight lines in accordance with the laws of light. This can be shown by experiments with screens and slits. Most solid bodies prevent or hinder the action, all metals and most insulators being opaque to it. Crystallised sugar, alum, calc-spar, and rock salt transmit the action, but with diminished intensity. Gypsum (selenite) and rock-crystal proved completely transparent. Amongst liquids pure water proved remarkably transparent, but the addition of a few drops of salt solution was sufficient in many cases to extinguish the passive spark. Paraffin, benzole, petrol, carbon bisulphide were almost opaque. Coal gas is notably opaque, and similar powerful absorption is shown by the brown vapours of nitrous oxide. Chlorine and the vapours of bromine and iodine exercise absorption, but not at all in proportion to their opacity.

The action of the active spark can be reflected from most surfaces, and the reflection takes place in accordance with the laws of light. Further, in passing from air into a solid transparent medium, refraction takes place as in the case of light, but the refraction is stronger than for light of the visible

* The passage of the discharge through the second circuit can be made evident to a large audience by inserting a Geissler vacuum tube in series with the spark-gap B,

spectrum. This result was obtained by the use of a prism of quartz and another of rock-salt. By examining the region in which the active spark exerted its influence, it was found that it corresponded with a deviation decidedly greater than the visible violet.

All these facts agree with the hypothesis that the cause of the action is the light of the active spark, and that the effective light belongs to the ultra-violet portion of the spectrum. If the hypothesis is correct, we should expect similar results from other sources of light. This expectation is easily realised, for an increase in the length of sparks from an induction coil is produced by bringing near a candle flame, using a quartz plate to prevent convection from the flame to the spark-gap.

The flames of gas, wood, benzene, &c., all act in the same way. Magnesium light produces a far more powerful effect, its action extending to a distance of about a metre. Lime-light, produced by means of coal gas and oxygen, acts up to a distance of half a metre; the action is mainly due to the jet itself. Sunlight gives no decisive effect. The electric arc is the most effective source of light, acting at a distance of 4 metres. The action proceeds chiefly from the violet light of the feebly luminous arc between the carbons. Most of the experiments already described were repeated, using the light of the electric arc. As regards rectilinear propagation, reflection, refraction, and absorption, the results obtained agreed with the former ones.

One other observation recorded by Hertz must be mentioned. The action on the passive spark takes place near the poles, more especially near the negative pole. Whether the effect was produced entirely at the kathode, or only chiefly at the kathode, could not be decided with certainty. Wiedemann and Ebert * investigated this point, and found that the seat of the action was the kathode.

Hallwachs † sought for other phenomena due to ultra-violet light which would serve to explain the results obtained by

* Wiedemann and Ebert, *Ann. der Physik*, **33**, p. 241, 1888.

† Hallwachs, *Ann. der Physik*, **33**, pp. 301-312, Jan. 1888.

Hertz. He examined the action of light from the electric arc on electrostatically charged bodies. A polished zinc plate was connected with a gold-leaf electroscope, and after having been charged, was illuminated by light from an arc lamp. If the charge was negative, the gold leaves commenced to collapse as soon as light fell upon the plate; if the charge was positive, no effect was produced. The action was found to be due principally to the ultra-violet rays, as in the experiments of Hertz. Similar results were produced by the light from burning magnesium ribbon.

The phenomenon was traced to an action of the light on the surface of the charged body. No action of the light on the medium (air) in which the body was placed could be detected. A polished zinc plate was from 40 to 50 times as active as an old plate of the same material. Iron was less active than zinc, and zinc less active than aluminium. Hallwachs concludes that, when a negatively electrified metal plate is illuminated, negatively electrified particles travel away from it and follow the lines of force of the electric field.

At the close of his article in the *Annalen* Hallwachs mentioned that "metal plates become electrostatically charged when irradiated with the electric light." This was confirmed shortly afterwards* by suspending a metal plate, connected with a Hankel's electrometer, inside an iron cylinder.

"The case was of rusty iron, so that the contact potential against the plates to be suspended was always negative. In this case only could the rises of potential indicated by the electrometer be indubitably explained. For if the plate had been negative to the case, a rise of negative potential would have occurred, due to the transport of negative electricity by the illumination. If the plate, however, was positive towards the case, and therefore possessed a positive charge, an increase of potential could only be due to the fact that positive electricity was produced on the plate by irradiation."

In the case of zinc, brass and aluminium with brightly polished surfaces, positive electricity occurred on irradiation.

* Hallwachs, *Göttinger Nachrichten*, May 1888; *Phil. Mag.*, 5, 26, pp. 78-80, July 1888.

The maximum potential with zinc amounted to over a volt, with brass to about a volt, and with aluminium to 0.5 volt.

As we have seen, Hallwachs merely connected the plate under examination to an electroscope. Righi and Stoletow almost at the same time devised a new method for studying the discharge of bodies charged to a low potential. They placed a metallic grating or net parallel to and a few millimetres away from the metallic plate. Righi connected the two conductors to the two pairs of quadrants of an electrometer. Stoletow connected the plate to the

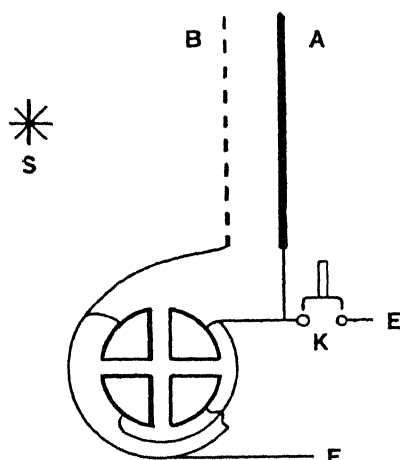


FIG. 2

negative pole of a voltaic pile, and the grating to the positive pole of the pile, inserting a sensitive galvanometer to measure the current.

Righi * placed a vertical metallic disc A (Fig. 2) not far from a parallel metal net B. A is in connection with one set of quadrants of an electrometer, B in connection with the other quadrants and with earth. If A is put to earth for an instant and then illuminated with magnesium light or the arc, a deflection is obtained, which reaches its maximum in a time which is shorter the nearer the irradiating source, and the larger the

* Righi, *R. Acc. dei Lincei*, March 4, 1888; *Phil. Mag.*, 5, 25, pp. 314-316, April 1888.

surfaces of the two metals. "The deflection is negative if A is zinc and B brass. The same final value is obtained if A is so initially charged as to have a greater deflection.

"If A is very near B, the complete deflection does not change if A is suddenly withdrawn from B, which proves that the radiation has reduced the two metals to the same potential. It follows that this deflection measures the difference of the potential of contact between A and B. If B is placed in connection with the electrometer instead of A, the deflection is of contrary sign."

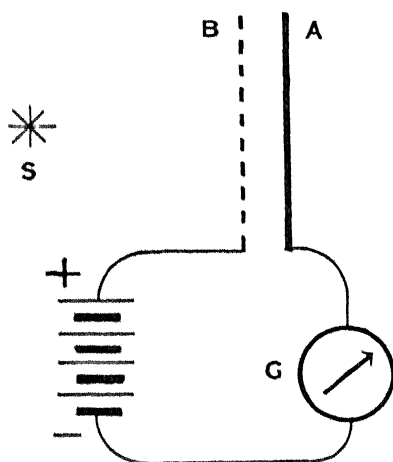


FIG. 3

The arrangement may be called a photo-electrical cell. A photo-electrical battery may be formed by joining such cells in series.

If the net in this experiment is taken away and the plate A is illuminated, "a deflection is slowly formed, which is positive with the bodies as yet studied."

"There is an electrical convection, provoked by ultra-violet radiations, from bodies on which exists an electrical distribution of a given sign (negative probably), caused by electromotive forces of contact, towards those on which exists an electrical distribution of contrary sign (positive) due to the same cause."

In Stoletow's arrangement the metal plate A is connected through a high resistance galvanometer of great sensitiveness to the negative terminal of a pile. The grating B is connected to the positive terminal of the pile (Fig. 3). When the plate is illuminated the galvanometer indicates the passage of a current, but if the connections are reversed no deviation of the galvanometer is produced. This would be the case if the plate gives out negatively electrified particles under the influence of light.

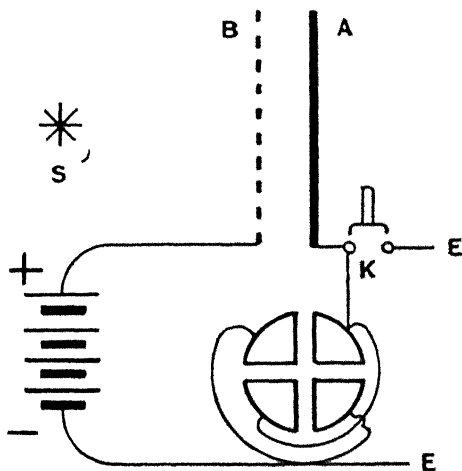


FIG. 4

Instead of the galvanometer a quadrant electrometer is frequently employed, as shown in Fig. 4.

Stoletow constructed a photo-electric cell by allowing ultra-violet light to pass through the openings of a perforated plate and fall upon a second plate. He came to the conclusion that the plate upon which the light fell must be of the less electro-positive metal, so that the contact difference of potential should drive negative electricity from the illuminated to the perforated plate.

The conclusions of Righi, Stoletow and Arrhenius* with regard to the formation of a photo-electric cell require some amplification. They regarded the current produced as due

* Arrhenius, *Wied. Ann. d. Physik*, **33**, p. 638, 1888.

solely to the contact difference of potential between the metals, and thought of the air between the plates as an electrolyte which reduced the two plates to the same potential. Although this contact difference of potential must be taken into account in estimating the effect produced, the main action is due directly to the light, which liberates negative charges from the illuminated plate, so giving it a positive potential. This positive potential may rise sufficiently to overcome the effect of the contact difference of potential, so that a current of negative electricity can flow from the more electropositive metal.* This is found to occur with the alkali metals.

A tube prepared by Fleming,† containing sodium-potassium alloy opposite a platinum electrode, gave rise to an electromotive force of 0.6 volt when illuminated by a concentrated beam of light from an arc lantern. The current through a galvanometer of resistance 180 ohms was found to be 5.4 microamperes. If the effective E.M.F. is the same when the circuit is open and closed, this would indicate an equivalent resistance of 74,000 ohms. Another cell showed an E.M.F. of 0.45 volt. If the two cells were placed in series they formed a photo-electric battery, and the E.M.F. was found to be 1.0 volt.

* See Ladenburg, *Ann. d. Physik*, **12**, p. 572, 1903.

† Fleming, *Phil. Mag.*, **17**, pp. 286-295, 1909.

CHAPTER III

THE EMISSION OF NEGATIVE ELECTRONS IN A VACUUM

THE existence of discrete electrical particles or atoms is suggested by the relations found by Faraday to hold good in electrolysis. If we express these results in terms of the atomic theory, we may say that the charge carried by a univalent ion is independent of the nature of that ion ; a divalent ion carries exactly twice, and a trivalent ion three times, this quantity of electricity. This is in agreement with the supposition that there is an electric atom associated with each univalent particle, and an appropriate number of such atoms with each particle of higher valency.

The theory of *electrons*—to use the term proposed by Johnstone Stoney to designate the elementary electrical quantity—has developed along independent but converging lines. Helmholtz and H. A. Lorentz, working independently, showed that it was possible to explain the dispersion of light in absorbing media on electro-magnetic principles, assuming the presence of such elementary charges. Larmor first showed the possibility of constructing an atom by means of moving electric charges. In 1896 Zeeman observed the broadening, and subsequently the resolution, of the spectral lines when the luminous source was placed between the poles of a powerful electro-magnet. Lorentz gave a theoretical explanation of the results on the assumption that the light had its origin in the vibration of electrons associated with the atoms of ordinary matter. The vibrating electron was found to be negatively charged.

Another line of investigation leading up to the electron theory was initiated by the experiments of Varley and Sir William Crookes on kathode rays. When a vacuum tube is

exhausted, the negative electrode is surrounded by a dark space, the extent of which increases as the exhaustion improves. If the dark space extend to the walls of the tube, a striking green phosphorescence is produced there. Crookes explained this by supposing a stream of negatively electrified particles, or "radiant matter," to be shot off from the electrode. Experiment showed that radiant matter travelled in straight lines, so that the interposition of a solid object caused the formation of a shadow on the walls of the tube. The stream of particles could produce heating and mechanical effects, and was deflected by a magnetic field.

In 1897 Professor J. J. Thomson (now Sir Joseph Thomson) showed that the particles in the kathode stream carry a charge of negative electricity, and completed the well-known experiments by which he determined the ratio of the charge e to the mass m , and also the velocity of the particles. The value of e/m , the ratio of the charge to the mass, was found to be about 10^7 E.M.U.,* and the velocity about one-tenth the velocity of light. In the case of the hydrogen atom in electrolysis, e/m is about 10^4 E.M.U. Thus the ratio was about 1000 times greater for the kathode particle than for the hydrogen atom. The charge e carried by the kathode particle had not been measured, but it was proved later that the charges carried by the ions produced by Röntgen rays were the same as those in electrolytic convection; consequently, if we assume e to be the same in these three cases, the negatively electrified particle, or "corpuscle," of the kathode stream must have a mass roughly 1/1000 (more accurately 1/1700) part of that of the hydrogen atom.

We turn now to photo-electric phenomena and their bearing on the electron theory. Experiment has shown that the discharge of negative electricity under the influence of light is the result of convection. The charge of the illuminated plate is carried away by negatively charged particles. At ordinary pressures the carriers move slowly and follow the lines of electrostatic force, but at low pressures

* The mean of a number of later determinations of e/m is 1.772×10^7 E.M.U. (Kaye and Laby, 1911.)

Righi* found that the velocity became larger and the path became straighter. At ordinary pressures the photo-electric discharge is unaffected by a magnetic field, but in a good vacuum, as Elster and Geitel† have shown, a magnetic field parallel to the charged surface greatly diminishes the photo-electric current. These results suggest that the photo-electric carriers ("photo-electric rays") in a vacuum are identical with the kathode particles ("kathode rays") in an ordinary Crookes tube. This conclusion was supported by further investigation. In 1899 J. J. Thomson‡ determined the ratio of the charge to the mass of the carriers of negative electricity, when a metal plate in a good vacuum is illuminated by ultra-violet light. The value found agreed within the limits of experimental error with that for the kathode particle. Further, the value of the charge e § was determined, and found to be in agreement with that of the elementary charge in electrolysis.

Shortly afterwards an independent investigation by a different method was published by Lenard, who also proved that the photo-electric current in a good vacuum was carried by slow kathode rays. These results were confirmed by the experiments of Merritt and Stewart. The three investigations referred to are of such fundamental importance in the history of the electron theory, and in showing the liberation of electrons by light, that they are described in some detail in the following pages.

THE EXPERIMENTS OF J. J. THOMSON

Determination of $\frac{e}{m}$.—The determination of $\frac{e}{m}$ involves a knowledge of the effect of a magnetic field on the path of an electrified particle moving in one plane.

Consider the motion of a particle of mass m , carrying a charge e , when there is a magnetic field of strength H perpen-

* Righi, *Mem. della Reale Acad. di Bologna*, (4) 9, p. 369, 1888.

† Elster and Geitel, *Wied. Ann. d. Physik*, 41, p. 166, 1890.

‡ J. J. Thomson, *Phil. Mag.*, 48, p. 547, 1899.

§ The mean of the later determinations of e is 4.7×10^{-10} E.S.U. = 1.57×10^{-20} E.M.U. (Kaye and Laby, 1911.)

dicular to the plane, and an electric field E in the plane of motion.

In consequence of the electric field there will be a mechanical force on the particle of amount Ee , and this will produce an acceleration $\frac{Ee}{m}$ in the direction of the field.

In consequence of the magnetic field there will be a mechanical force on the particle of amount Hev , where v is the velocity of the particle at any instant. This force acts at right angles both to the magnetic field and to the direction of motion, and will produce an acceleration Hev/m .

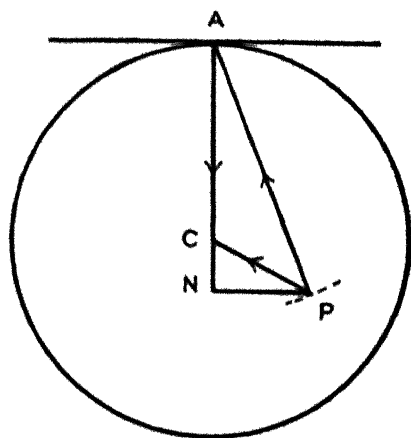


FIG. 5

By writing down and integrating the equations of motion, it can be shown that, when the particle is liberated without appreciable velocity, the path it describes is a cycloid. Professor W. B. Morton* has given an elegant elementary proof of this result.

Let the circle in the figure roll along the horizontal straight line with constant angular velocity ω . Then at any instant the point of contact A of the circle with the line on which it rolls is at rest. A is the point of zero velocity. The centre C traces out a straight line with constant velocity. C is the point of zero acceleration.

* W. B. Morton, *Proc. Phys. Soc. Lond.*, **21**, p. 300, 1909.

The velocity of P, any point in the plane of the circle, is its velocity relative to A ωAP in a direction perpendicular to AP.

The acceleration of P equals its acceleration relative to C $= \omega^2 PC$ along PC.

This may be resolved into two components :

$$\begin{aligned}\omega^2 PA \text{ along PA} &= \omega v \text{ along PA,} \\ \omega^2 AC \text{ along AC} &= \omega^2 a = a \text{ constant.}\end{aligned}$$

The first component is perpendicular to the direction of motion, and may be identified with the acceleration due to a magnetic field perpendicular to the plane of the diagram.

The second component may be identified with the acceleration due to an electric field parallel to AC.

Hence

$$\omega v = H e v / m,$$

$$\omega^2 a = E e / m.$$

Thus ωa which is equal to the velocity of C $= E/H$,

$$\text{and } a = E m / H^2 e.$$

So we see that, in the general case of a particle projected in any manner in a plane perpendicular to the magnetic field, the path is given by the point P on the rolling circle—in other words, the path is a trochoid. When the point P is on the circumference of the circle, its velocity vanishes when it is at the point of contact with the fixed line. In this case the path is a cycloid.

Suppose a metal plate AB, Fig. 6, is placed parallel to and a small distance away from a larger metal grating CD, so that it can be illuminated by ultra-violet light passing through the meshes. If an electric field is applied so that the particles emitted by AB are urged towards the grating, the rate at which CD receives a negative charge can be measured by a quadrant electrometer. When a transverse magnetic field is applied at the same time as the electric field, a particle emitted from AB with a negligible velocity would describe a cycloid. If this cycloid intersects the grating CD, the particle would give up its charge to the quadrants in connection with the grating;

but if the distance between AB and CD is increased to a value greater than the height of the cycloid, the particle would never reach CD. Thus we should expect a sudden diminution in the rate of leak when the distance between AB and CD becomes greater than $2a = 2Em/H^2e$.

In an actual experiment the distance between the plates was fixed and the strength of the electric field was varied,

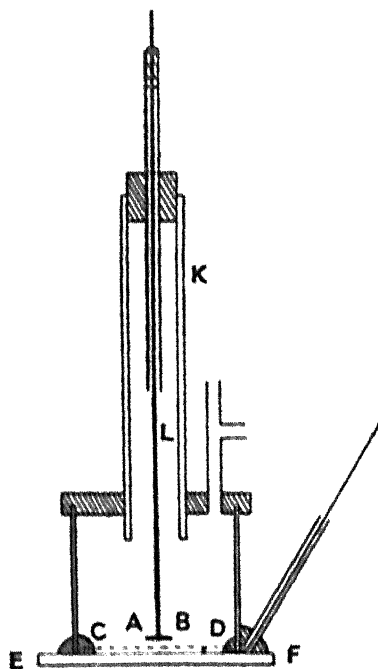


FIG. 6

so as to find the strongest field at which any effect due to the magnetic field could be detected.

The simple theory indicates an abrupt transition from the case when the magnetic field produces no effect, to that in which it entirely stops the flow of negative electricity to CD. This abrupt transition was not realised in practice. In order to explain this result Thomson supposed that the ions were not formed exclusively at the surface of the metal, but throughout a thin layer of gas in contact with the plate, in consequence

diagram was connected to the apparatus for producing the sudden expansion.

In order to obtain consistent results the intensity of the light used must be small. The light passed upwards through the base of the vessel—a quartz plate about .5 cm. thick—then through a layer of water about 1 cm. thick, and fell on the zinc plate, which was 1.2 cm. above the water.

The mean value of e was 6.8×10^{-10} E.S.U.

THE EXPERIMENTS OF LENARD

Experiments carried out by P. Lenard* about the same time led him to the conclusion that an emission of kathode rays takes place in a high vacuum under the influence of ultra-violet light. Earlier experiments had suggested that heavy material particles might be the carriers of electricity, but further investigation showed that this explanation was not sufficient. For example, a surface of sodium amalgam in hydrogen gave out 2.9×10^{-6} coulombs of negative electricity on being illuminated for some time, yet no sodium could be detected on a charged platinum wire placed near it.

Lenard first examined the relation between the photo-electric current and the potential difference when the illuminated surface was in a high vacuum. The results are shown in the following table :

Potential of Illuminated Electrode.	Electricity Discharged.
- 45000 volts	24.5×10^{-10} Coul./Sec.
- 25000	26.6
- 8900	22.5
- 4100	24.8
- 1300	24.5
- 500	23.4
- 120	21.9
- 14	19.9
- 9	15.9
- 1	7
0	4
+ 1	4
+ 2.1	0

* Lenard, *Annalen der Physik*, 4, 2, pp. 359-375, 1900.

1. In the first part of the table the quantity of electricity discharged is independent of the potential. (This potential was not of itself sufficient to produce any discharge.)

2. When the potential falls below 100 volts the quantity diminishes. Lenard explains this by supposing that, when the potential difference is insufficient, part of the electricity already liberated by the light returns again to the electrode.

3. In the third part of the table the quantity discharged falls to zero for a positive potential of 2.1 volts, which is the same as the insulated plate would attain when illuminated by ultra-violet light.

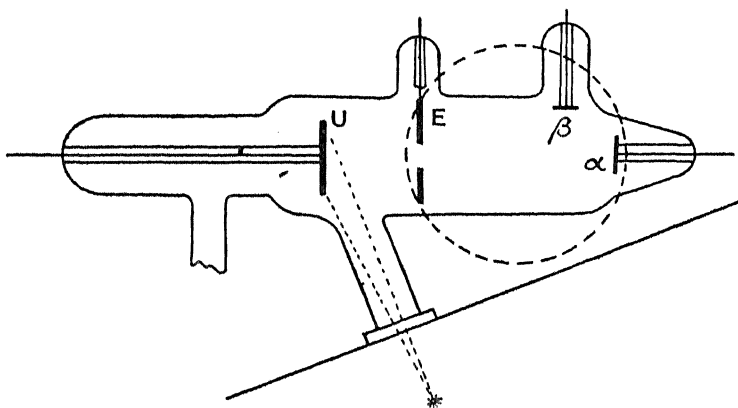


FIG. 8

The vacuum tube employed in these experiments is illustrated in the diagram, Fig. 8.

The aluminium electrode U was illuminated by light from a spark between zinc terminals, through the quartz window B. The electrode E, which was connected to earth, was provided with an aperture 5 mm. wide through which the photo-electric rays passed. When there is no magnetic field α receives a negative charge.

By passing a current through coils, indicated by the dotted circle, placed on either side of the tube, β receives a charge while α does not. This is what we should expect if cathode rays started from U and travelled down the tube.

Let P denote the potential of the illuminated electrode in electromagnetic units,

v_0 – velocity of particle on leaving the electrode,

v – velocity acquired in the electric field.

$$\text{Then } \frac{1}{2} m (v^2 - v_0^2) = Pe.$$

In a magnetic field H the particle describes a curve of radius

$$R = \frac{v}{H} \cdot \frac{m}{e}.$$

Putting $H = H_1 C$ where C is the current through the coils in amperes and H_1 the field due to one ampere, we get

$$\frac{P}{C^2} = \frac{1}{2} H_1^2 R^2 \frac{e}{m} = \text{a constant}$$

assuming the initial velocity v_0 is small.

The following table gives the experimental results :

P	C	$\frac{P}{C^2}$	$\frac{e}{m} = \frac{P}{C^2} \cdot \frac{2}{H_1^2 R^2}$	$v = \frac{2P}{H_1 R C}$
607×10^8	0.65	144×10^9	11.7×10^6	0.12×10^{10}
4380	1.78	138	11.2	0.32
12600	2.94	146	11.8	0.54

The initial velocity of the particles can be determined from a knowledge of P_0 , the positive potential (2.1 volts) which the electrode must have to cause the particles to return to it.

For

$$\frac{1}{2} m v_0^2 = P_0 e$$

$$v_0 = \sqrt{2 P_0 e / m}$$

This gives

$$v_0 = 10^8 \text{ cm./sec.}$$

These experiments show that in a vacuum cathode rays (negative electrons) are given off by the illuminated surface.

THE EXPERIMENTS OF MERRITT AND STEWART

Merritt and Stewart* carried out experiments showing "the development of cathode rays by ultra-violet light" about the same time as Lenard. Their experiments on the

* Merritt and Stewart, *Physical Review*, 11, pp. 230-250, 1900.

magnetic deflectability of the photo-electric rays are similar to those of Lenard, and, like the latter, give a *direct* proof that the rays are deflected by a magnetic field. The apparatus used is shown in Fig. 9.

The kathode K of zinc was at the bottom of the tube, the anode A being a ring of aluminium. The kathode was illuminated by light from a spark between zinc terminals coming through the quartz window Q. The kathode was kept at a potential of about 1000 volts by means of a dry pile.

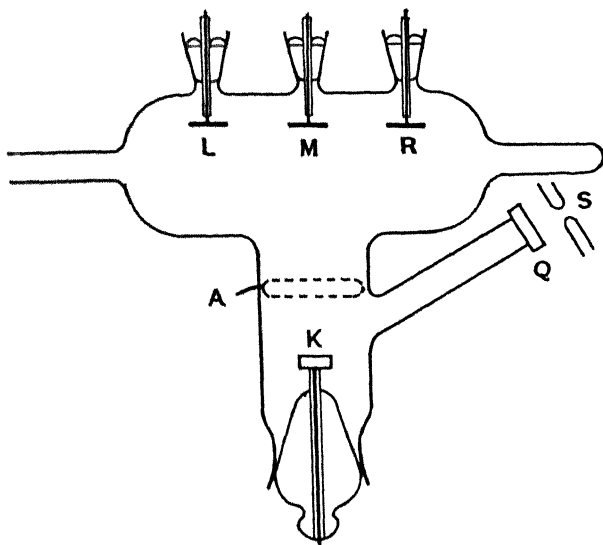


FIG. 9

The three electrodes, L, M, R, were fixed at the top of the tube, and the rate of change of potential could be measured by a Kelvin quadrant electrometer.

With no magnetic field M received a negative charge. When a weak magnetic field was applied at right angles to the plane of the diagram and directed away from the observer, the charge received by R was increased while that received by M was diminished. When the field was reversed the charge received by M was the same as in the previous case, but the increased charge was now found at L instead of at R. In order to obtain a sharply marked effect the strength of the

magnetic field must lie between rather narrow limits. These results show that the photo-electric rays are magnetically deflected, and the deflection corresponds with that observed in the case of kathode rays.

The deflection produced depends on the potential of the kathode, the photo-electric rays becoming "stiffer" as the potential of the kathode is increased.

Merritt and Stewart formed the opinion that, in addition to the charged particles similar to those in the kathode rays, heavier and more sluggish ions are also present. These are attributed to the ionisation of the residual gas in the tube. They suggest that the presence of these slowly-moving ions affords an explanation of the partial discrepancy between theory and experiment in Thomson's work.

CHAPTER IV

THE VELOCITY OF THE ELECTRONS

HAVING proved that corpuscles or electrons are liberated in a vacuum when a polished metal plate is illuminated by ultra-violet light, we proceed to consider in the present chapter the methods that have been employed to measure the velocity of emission.

We have seen that Lenard measured the initial velocity by finding the positive potential that must be given to the electrode to prevent the electrons from leaving it. This gives us information only as to those electrons whose velocity is a maximum. It is desirable to investigate the case of those electrons which are emitted from the electrode with velocities less than this maximum. For this purpose we require to know the form of the "velocity distribution curve."

VELOCITY DISTRIBUTION CURVES

We consider first the classical experiments of Lenard * to determine the variation of the quantity of electricity discharged in a high vacuum with the potential difference applied. The illuminated plate U (Fig. 8) was of aluminium coated with turpentine black. The following table illustrates the results obtained. In the first part of the table the potential difference was applied so as to increase the velocity of the electrons leaving the plate U, in the second part the electric field tended to drag them back to the plate.

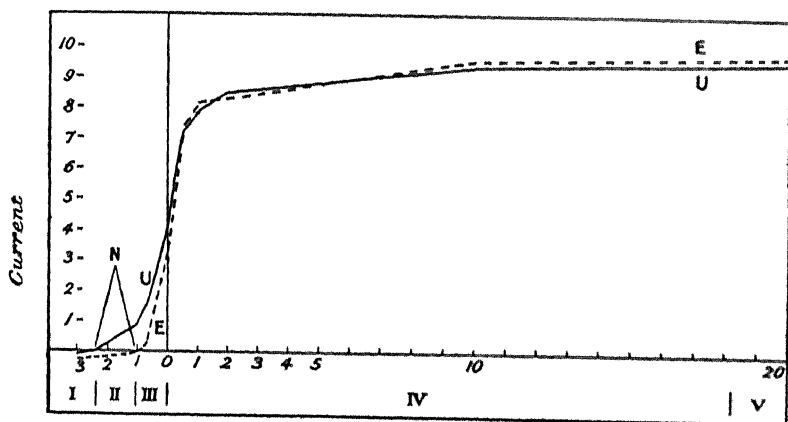
* Lenard, *Ann. d. Physik*, 8, pp. 149-198, 1902.

Variation of Quantity of Electricity with Potential Difference

Distance $UE = 10$ mm.

Accelerating Force (Carbon Arc, also Sparks).			Retarding Force (Carbon Arc).		
P.D. in Volts.	Discharge from U.	Charge reaching E.	P.D. in Volts.	Discharge from U.	Charge reaching E.
X	U	E	X	U	E
100	1.00	1.00	-0.66	0.162	0.029
10	0.94	0.96	-0.8	...	0.0094
2	0.85	0.84	-1.0	0.082	0.000
1	0.79	0.81	-1.2	...	-0.0041
0.5	0.73	0.74	-1.4	...	-0.0065
0.3	0.65	...	-1.8	...	-0.0072
0.2	0.55	...	-2.4	0.0000	...
0	0.40	0.34	-3.0	-0.0026	-0.0071

If these results are plotted, taking potentials as abscissæ and quantities of electricity as ordinates, we obtain the curves shown in the figure, where the continuous line represents the



Potential Difference

FIG. 10

charge leaving U and the dotted line represents the charge reaching E. Such curves are called velocity distribution curves. In these curves we may distinguish five stages,

which are indicated by the Roman numerals at the base of the diagram.

I. With a large retarding field, electrons leaving U under the influence of the light are dragged back again before they have travelled an appreciable distance from the plate. In this stage both U and E would have zero values, were it not for some light being reflected from U to E and producing a small discharge from E to U. Consequently E and U are negative.

II. In the second stage, with a smaller retarding field, electrons are able to escape from U but do not reach the plate E. Consequently U has a small positive, E a small negative value.

III. When the retarding field is still smaller, some of the electrons emitted from U reach the plate E instead of the glass walls of the apparatus, and E assumes a positive value.

IV. When an accelerating field is applied the two curves practically coincide.

V. In the final stage, with a large accelerating field, the two curves become nearly horizontal.

It will be seen that the effects are complicated by light reflected from the surface of the electrode U and falling upon E. The fraction of the incident light so reflected was estimated in various cases. It depends on the source of light and the surface of the electrode. When this fraction is known, the observed curve can be corrected so as to give results free from the influence of reflected light.

Such a curve will have a null point for a certain value of the retarding field. The potential difference is then just sufficient to destroy the velocity of those electrons which are emitted with the greatest velocity. For any retarding field the photo-electric current may be taken as a measure of the number of electrons possessing velocities greater than that which corresponds to the particular potential difference. If V is the potential difference just sufficient to destroy a velocity v , we have $\frac{1}{2}mv^2 = Ve$, or $v = \sqrt{2Ve}$. If V is measured in volts, this means $v = \sqrt{2 \times 10^8 V}$ cm./sec. Thus, taking

$e/m = 5.3 \times 10^{17}$ E.S.U., the velocity $v = 5.95 \times 10^7$ cm./sec., for $V = 1$ volt.

Lenard calculated the relative number of corpuscles emitted with any assigned velocity from plates of carbon, platinum and aluminium.

	Carbon.	Platinum.	Aluminium.
Corpuscles emitted with velocities between—			
12 and 8×10^7 cm./sec.	0.000	0.000	0.004
8 and 4×10^7 cm./sec.	0.049	0.155	0.151
4 and 0×10^7 cm./sec.	0.67	0.65	0.49
Corpuscles emitted only with an external field	0.28	0.21	0.35
	1.00	1.00	1.00

The velocity distribution curves obtained experimentally are liable to distortion from several causes besides that due to light reflected from the illuminated plate.

O. v. Baeyer* pointed out that electrons may undergo

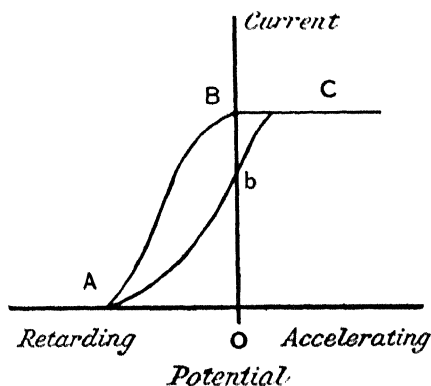


FIG. 11

reflection from the sides of the case even when travelling with small velocities. In order to prevent these reflected electrons from reaching the plate under test, he suggested the use of

* O. v. Bayer, *Verh. d. Deutsch. Phys. Ges.*, 10, p. 96, 1908.

a perforated screen and an auxiliary field. Ladenburg and Markau* protected the receiving plate by means of a shield of wire gauze which was given a permanent negative charge. The effect of reflection of electrons on the velocity distribution curve is illustrated in the figure (Fig. 11). If the illuminated plate emits electrons with velocities ranging from a maximum down to zero, a curve such as ABC would be obtained. The curve, as modified by the reflection of electrons, would be *AbC*. When the plate and the case are at the same potential, *Ob* would represent the actual photo - electric current, *bB* the current of electrons reflected back from the case. Two of the curves obtained by Ladenburg and Markau are reproduced in Fig. 12. Curve I was obtained with, and curve II without the use of the negatively charged gauze.

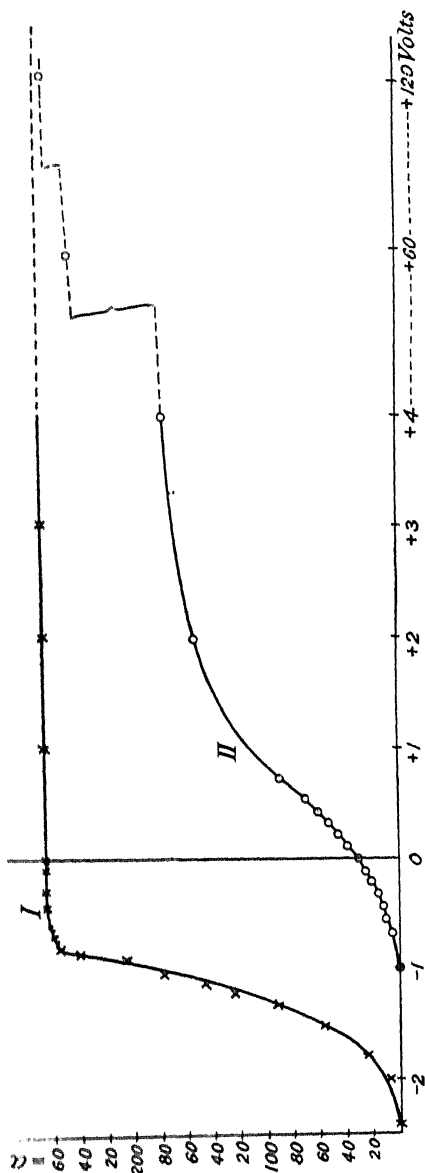


FIG. 12

When an auxiliary field is used, it produces a shift of the

* Ladenburg and Markau, *Phys. Zeitschr.*, **9**, pp. 821-828, 1908; *Verh. d. Deutsch. Phys. Ges.*, **9**, p. 562, 1908.

curves to the left which cannot be attributed to the prevention of reflection.* There is another factor contributing to the alteration of the curve—namely, the stray field through the perforated screen. This shift can be calculated and corrected for.

A simple method of eliminating errors due to the reflection of electrons, without using an auxiliary field, has been devised by Richardson and Compton.† This is described in Chapter X.

Hughes‡ has pointed out that, whenever an electron approaches a boundary obliquely, then the potential difference just necessary to stop it is less than that potential which corresponds to its actual velocity. The velocity distribution

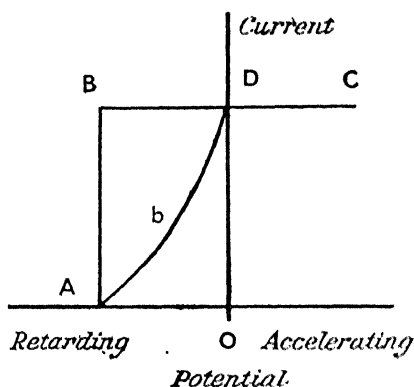


FIG. 13

curve for electrons leaving a point with equal velocities, instead of being ABDC, would be A δ DC, Fig. 13.

Hughes has also examined the effect of weak magnetic fields (such as the earth's field) on the form of the curve. Some of the slower electrons would describe curved paths in the magnetic field and never get away from the illuminated plate. This point was investigated experimentally by applying a magnetic field so as to assist or oppose the earth's field. It was found that, for velocities corresponding to a fall of potential of 0.7 volt (and above), the effect of the earth's field (.5 Gauss) on the maximum velocity can be ignored.

* Compton, *Phil. Mag.*, **28**, pp. 579-593, 1912.

† Richardson and Compton, *Phil. Mag.*, **24**, pp. 575-594, 1912.

‡ Hughes, *Phil. Trans. Roy. Soc.*, **212**, pp. 205-226, 1912.

In estimating the value of the potential difference for a velocity distribution curve, it is necessary to take into account any contact difference of potential that may be present owing to the use of different materials for the illuminated plate and the surrounding case. Attention has been drawn to the importance of this correction by K. T. Compton.* The electrons moving between the emitting and receiving plates are acted on by the force due to the contact difference of potential, as well as by the externally applied field. The curve for the electropositive metal falls to the left of the curve for the electronegative. By displacing the curves through a distance equal to the measured contact difference of potential the curves for different metals become nearly identical, showing that different metals, when illuminated with ultra-violet light from an iron arc, give off electrons with practically equal velocities. We shall see later that the velocities for different metals are not exactly equal.

THE PRESENCE OF A SUDDEN BEND IN THE VELOCITY DISTRIBUTION CURVE

In his communication to the *Annalen der Physik* in 1902, Lenard mentions that he found experimentally a sharp bend in the velocity distribution curve in the neighbourhood of the axis of zero volts. This he explained theoretically as being due to the existence of surface forces acting upon the electrons only when they were within a small distance of the surface. His theory indicated that the curve should consist of two distinct branches meeting each other nearly at right angles.

Singularities of this kind are to be noticed in the curves obtained by A. Lienhop † in the course of his investigation on photo-electric action at low temperatures. They are present both in the curves for ordinary temperatures and in those for the temperature of liquid air.

On the other hand, Ladenburg and Markau ‡ found the

* K. T. Compton, *Phil. Mag.*, **23**, pp. 579-593, 1912.

† Lienhop, *Ann. d. Phys.*, **21**, pp. 281-304, 1906.

‡ Ladenburg and Markau, *Phys. Zeitschr.*, **9**, p. 821, 1908; *Verh. d. Deutsch. Phys. Ges.*, **10**, p. 562, 1908.

sharp bend in the curve vanished when reflection of electrons was prevented. In order to avoid such reflection they used in one experiment an auxiliary field and in another a Faraday cylinder, and found the same result in both experiments.

A. Klages * made a special examination of the velocity distribution curves for mercury and for zinc amalgam in the neighbourhood of zero potential, and came to the conclusion that there was a sharp bend present even when the reflection of electrons was prevented.

In order to explain these contradictory results special experiments were carried out by Gehrts,† who used a copper

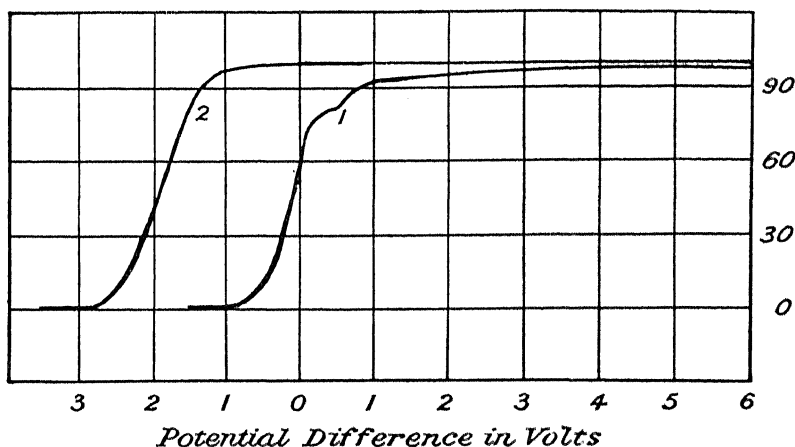


FIG. 14

plate as kathode. By increasing the distance between the illuminated plate and the plate receiving the electrons in a suitably designed apparatus, it was possible to diminish gradually the effect due to reflection. When this was done it was found that the bend in the velocity distribution curve became less and less distinct, and finally vanished altogether when the distance between the plates was made sufficiently great.

O. v. Baeyer and A. Gehrts ‡ examined the velocity distribution curves obtained with a surface of soot, when the

* A. Klages, *Ann. d. Phys.*, **31**, pp. 343-364, 1910.

† Gehrts, *Ann. d. Phys.*, **36**, pp. 1016-1026, 1911.

‡ v. Baeyer and Gehrts, *Verh. d. Deutsch. Phys. Ges.*, **12**, p. 870, 1910.

apparatus was so arranged as to diminish any effect due to reflection of electrons by increasing the distance between the illuminated plate and the reflector.

Curve I shows the velocity distribution curve when reflection takes place. There is a distinct bend in this curve for a field just greater than zero. The maximum initial velocity given by the curve corresponds to 1.2 volts.

Curve II corresponds to the case when the effect of reflection is diminished by increasing the distance from 7 mm. to 90 mm. There is no sharp bend in this curve, which gives an initial velocity corresponding to a fall of potential of 2.7 volts.

As Hughes has pointed out, it is difficult to see why reflection of electrons should influence the maximum initial velocity.

THE RESULTS OF EXPERIMENTS ON THE VELOCITIES OF PHOTO-ELECTRONS

We shall consider in later chapters the application of these velocity distribution curves to the discussion of the influence of temperature and of illumination on the photo-electric effect, but it will be convenient to mention at this point some of the investigations on the forms of the curves, and the initial velocities of the electrons.

The difficulty of obtaining a perfectly clean surface in a vacuum was overcome by A. Klages,* who experimented with a surface of mercury or of an amalgam, which could easily be renewed even in a high vacuum. The velocity distribution curves for mercury and for zinc amalgam gave values for the maximum initial velocity which were nearly the same. When a quartz mercury lamp was used as a source of light, this value corresponded to a potential difference of 2.3 volts. When a plate of calc-spar was placed in front of the quartz window of the apparatus, the velocity fell to a value corresponding to 1.5 volt. The maximum photo-electric current obtained from mercury was practically the same as that obtained from zinc amalgam or from tin amalgam.

* A. Klages, *Ann. d. Phys.*, **81**, pp. 343-364. 1910.

Experiments were carried out by v. Baeyer and Gehrts* with copper, silver, and gold. The investigators found that the condition of the surface had very marked influence on the initial velocity of the electrons, as well as on the number discharged. Fatigue effects were much in evidence in these experiments, and were attributed to the presence of gaseous films. The initial velocity determined when the surface was as clean as possible corresponded to a potential difference of 6.3 volts. This value is in fair agreement with the value calculated from the Planck-Einstein theory (Chapter XI) for a wave-length of $200\ \mu\mu$.

Richardson and Compton† have obtained interesting results from velocity distribution curves in the case of the metals platinum, aluminium, zinc, bismuth, magnesium, tin, and copper. In these experiments the metal surface was scraped with a clean knife-blade before the exhaustion of the vessel in which the test was carried out.

An important advance in the study of photo-electric phenomena was made by A. L. Hughes,‡ who showed how to obtain perfectly clean metallic surfaces free from gaseous films by distillation of the metal in a very high vacuum. The metals calcium, magnesium, cadmium, zinc, lead, bismuth, antimony, arsenic, and selenium were examined, and the maximum initial velocities of the electrons from them determined.

The results of all these experiments will be considered in connection with the influence of the wave-length of the light on photo-electric effects.

THE DIRECTION OF EMISSION OF PHOTO-ELECTRONS

If a flat metal plate is illuminated from the front, it is of interest to determine how the emission of electrons depends on the angle of emission. It is not to be expected that all the electrons should leave the plate in the direction of the normal to the surface. Lenard,§ in fact, observed that the

* v. Baeyer and Gehrts, *Verh. Deutsch. Phys. Gesell.*, **12**, p. 870, 1912.

† Richardson and Compton, *Phil. Mag.*, **24**, pp. 578-594, 1912.

‡ Hughes, *Phil. Trans. Roy. Soc., A*, **212**, pp. 205-226, 1912.

§ Lenard, *Ann. d. Phys.*, **2**, p. 359, 1900; **8**, p. 159, 1902; **12**, pp. 453, 777, 1903.

electrons leave the surface in different directions. Hughes * came to the conclusion that the emission is the same for all angles, but this is not in harmony with measurements carried out by Robinson † on different metals for the special purpose of examining this point. These measurements were undertaken in order to test a theory put forward by Riecke, who assumed that the emission of electrons from an element of the surface was the same for all directions included within a certain limiting cone. The experiments proved that the emission is a function of the angle of emission from the electrode. For small values of this angle the emission is considerable; it diminishes as the angle increases. The emission has been followed up to an angle of 75° , and it appears possible that emission may take place almost up to 90° .

THE EMISSION OF ELECTRONS FROM THIN METAL FILMS

The Photo-electric Effect with Incident and Emergent Light.—

In 1889 Hallwachs ‡ observed that thin silvered quartz plates showed photo-electric action when the plate was illuminated from the quartz side. Rubens and Ladenburg § examined the photo-electric properties of thin gold leaf (thickness 80 to 100 $\mu\mu$). They found that the ratio of the effect at the back to that at the front was about 1 to 100 for the thickness mentioned. The ultra-violet light transmitted by the gold leaf only amounted to about $1/1000$ of the incident light. From these observations the authors conclude that electrons are liberated in the thickness of the leaf with such velocities that many of them are able to escape from the back of the film.

The photo-electric properties of thin metallic films formed by means of deposition from a platinum kathode have been examined by Dike. || The film on glass is photo-electrically active even when of the utmost tenuity (down to 10^{-8} cm. in thickness). The high positive potentials observed by Dike

* Hughes, *Phil. Trans.*, A, **212**, p. 205, 1912.

† Robinson, *Ann. d. Phys.*, **31**, pp. 769–822, 1910.

‡ Hallwachs, *Tagebl. des Heidelberger Naturf.-Ver.*, p. 24, 1890.

§ Rubens and Ladenburg, *Deutsch. Phys. Gesell. Verh.*, **9**, pp. 749–752, 1908.

|| Dike, *Phys. Rev.*, **32**, pp. 631–632, 1911.

are probably to be attributed to imperfect screening from electrical waves.

The difference in the photo-electric effect caused by incident and emergent light has been examined by Otto Stuhlmann.* Thin metal films were prepared by "sputtering" in vacuo from a kathode. The ratio of the emergent (E) to the incident effect (I), determined from measurements of the ionisation currents in air, was found to be as follows :

	E/I.	Atomic Weight.
Magnesium	1.03	24.4
Iron	1.02	55.9
Copper	1.08	63.6
Zinc	1.11	65.3
Silver	1.07	107.9
Tin	1.15	118.5
Platinum	1.17	194.8
Lead	1.12	206.9

There appears to be a periodic variation of this "forward effect" with the change in the atomic weight.

Independent experiments carried out by Kleeman † led to the same conclusion as to an asymmetry of the effect for incident and emergent light. Experiments were made with platinum films in air at atmospheric pressure, and also in a good vacuum. It is suggested that the electrons receive a component of velocity in the direction of propagation of the light.

Measurements have been carried out with thin films of platinum in a high vacuum by J. Robinson.‡ For very thin films the velocities of the electrons for emergent light are greater than those for incident light; for thicker films the reverse is the case. The greatest thickness of film employed is estimated as 10^{-6} cm. For the thin films the maximum emergent current is larger than the maximum incident current; for the thick films this order is reversed. Thus for a certain

* Stuhlmann, *Phys. Rev.*, **32**, p. 621, 1911; *Phil. Mag.*, **20**, pp. 331-339, 1910; **22**, pp. 854-864, 1911.

† Kleeman, *Proc. Roy. Soc.*, **84**, pp. 92-99, 1910.

‡ J. Robinson, *Phil. Mag.*, **23**, pp. 542-551, 1912; **25**, pp. 115-132, 1913.

thickness of film the "emergent" velocity is equal to the "incident" velocity, and special experiments showed that for the same thickness of film the "emergent" current is equal to the "incident" current. The dissymmetry observed in the case of the velocities is not so strongly marked as that observed for the currents. The orientation of the plane of polarisation of the light did not have any influence on the dissymmetry.

Another striking result obtained in the course of these experiments was the fact that a sudden increase took place in the actual magnitude of the photo-electric currents, both for incident and emergent light, when the thickness of the film was 10^{-7} cm. For films thinner than this the ratio E/I was found to be practically constant, and equal to about 1.22.

Robinson has discussed various suggested explanations of the variation in the magnitude of the photo-electric current with the thickness of the film, and inclines to the view that the photo-electrons may possess sufficient energy to ionise molecules of platinum by colliding with them. If the thickness of the film is less than a certain quantity, which may be called the mean free path of the electrons, the only electrons present will be those produced directly by the light. If the film is thicker than this critical value, there will be present also electrons produced by collision between photo-electrons and molecules. From measurements of the Hall effect Paterson* estimated the mean free path of the electrons in platinum as of the order of 10^{-7} cm. This is in agreement with Robinson's view.

Partzsch and Hallwachs† have examined the optical and photo-electric properties of thin platinum films formed by cathodic deposition, and have come to the conclusion that the difference between the "incident" and the "emergent" photo-electric current can be accounted for by a difference in the reflecting power for light of the two sides of thin films. When such a film is illuminated from behind, as much as 40

* Paterson, *Phil. Mag.*, **4**, p. 652, 1902.

† Partzsch and Hallwachs, *Ber. Math.-Phys. Klasse Königl. Sächsischen Gesell. Wiss.*, **64**, pp. 147-166, 1912.

per cent. more light may be absorbed in the film than when the film is illuminated from the front. Consequently a greater photo-electric current is to be expected, and is actually found, when the light emerges from the film. Although the greater part of the difference between the "incident" and the "emergent" current may probably be accounted for in this way, the difference observed between the "incident" and the "emergent" velocity shows, in the opinion of the author, that there must be some influence at work tending to make the electrons leave the molecules more readily in the direction in which the light is travelling.

CHAPTER V

THE PHOTO-ELECTRIC CURRENT IN GASES AT VARIOUS PRESSURES

IN the preceding chapter we have seen that in a high vacuum the photo-electric current consists of a stream of negative electrons; these electrons are identical with those in the kathode rays of a Crookes' tube, but their initial velocity is smaller, being, as a rule, not much greater than 10^8 cm. per sec. The electrons travel in straight lines through the vacuum, except when they are under the influence of a transverse magnetic field.

We have now to deal with the processes taking place when the illuminated plate is in air or in some other gas. The fundamental fact is that discovered by Hallwachs—namely, the loss of charge from a negatively charged metal plate when illuminated by ultra-violet light. To explain this we assume that negative electrons are liberated from the metal under the influence of light, not only in a vacuum, but also in a gas at ordinary pressures. At atmospheric pressure the free electrons soon become attached to molecules of the gas, and thus form centres round which other molecules may collect, so as to produce negatively charged ions, which move with comparatively small velocities under the action of the electric field. Thus the discharge of the illuminated plate is attributed to a process of convection, in which negatively charged particles of molecular dimensions follow the lines of force of the electrostatic field.

The properties of the negative ions formed in gases by illuminating a metal plate with ultra-violet light have been investigated by several physicists.* Rutherford† measured

* See J. J. Thomson, *Conduction of Electricity through Gases*.

† Rutherford, *Proc. Camb. Phil. Soc.*, **9**, p. 401, 1898.

the velocity of the ions by applying an alternating electric field, and found the following values for the velocities under a potential difference of one volt per centimetre :

Gas.	Ionic Velocity.
Air	1.4 cm./sec.
Hydrogen	3.9 cm./sec.
Carbonic acid78 cm./sec.

Down to pressures of 34 mm. of mercury, the ionic velocity was found to be inversely proportional to the pressure of the gas. The effect of changes in pressure and temperature upon the velocity of the ions has been further studied by Kovarik.* Townsend † found the coefficient of diffusion of these negative ions to be .043 in dry air and .037 in moist air, values practically identical with those found for negative ions produced by Röntgen rays or radio-active radiations. The rate at which these ions diffuse through a gas is small compared with the rate at which the molecules of one gas diffuse through another, suggesting that several molecules condense round an electron to form a single ion.

So far we have been assuming that the pressure of the gas is not far from atmospheric, and that only moderate electric fields are employed. When the pressure is reduced, or when the strength of the field is increased, fresh possibilities are introduced which greatly complicate the phenomena. Under certain conditions the electrons may have their velocity augmented to such a degree as to produce ionisation by collision with the molecules of the gas, so giving rise to both positive and negative ions. When this occurs, instead of having carriers of only one sign present, carriers of both signs will be available, which will move in opposite directions through the field. By increasing the strength of the field still further the positive ions can bring about ionisation by collision, but this occurs only when the potential difference applied is not far short of that required to produce a spark through the gas.

* Kovarik, *Phys. Rev.*, **30**, pp. 415-445, 1910.

† Townsend, *Phil. Trans.*, A, **195**, p. 259, 1900.

Thus we see that the photo-electric current may arise in three ways : (1) The current may be carried by the electrons liberated by the ultra-violet light ; (2) the current may be carried by the ions formed by the adhesion of gaseous molecules to these electrons ; (3) the current may be carried by ions produced by collision. The relative proportions of the current carried in these three ways will depend on the pressure of the gas and the strength of the electric field. In a good vacuum practically the whole current is carried by negative electrons. As the pressure is increased, less current is carried by electrons and a larger proportion by negative ions, and at atmospheric pressure the electrons form such ions within a very small distance of the illuminated surface, so that the whole current is then carried by ions. When, however, the electric field is sufficiently increased, the actual value depending on the pressure of the gas, ionisation by collision begins to take place, and ions of both signs are produced. The negative ions move, as before, to the anode, while the positive ions formed make their way to the kathode, and are there discharged.

The remainder of the chapter gives a more detailed discussion of these processes. We consider first the case in which only moderate electric fields are employed, so that ionisation by collision does not occur. The mathematical theory of the conduction of electricity by negative ions is first dealt with, and then the experimental work on the variation of the current with the potential difference at various pressures is described. The latter part of the chapter is concerned with the more complicated relations that arise when ionisation by collision takes place.

MATHEMATICAL THEORY OF CONDUCTION BY NEGATIVE IONS

The first question to be considered is the way in which the strength of the electric field is affected by the presence of negatively charged particles between the electrodes. The result may be obtained by employing

the well-known equation of Poisson, which may be written

$$\frac{dX}{dx} + \frac{dY}{dy} + \frac{dZ}{dz} = 4\pi\rho,$$

where X , Y , and Z are the components of the electric field, parallel to the co-ordinate axes at a point (x, y, z) , and ρ is the density of the free electrification at that point.

Now consider the case in which the potential varies only with x , as when dealing with two infinite parallel plates.

Then
$$\frac{dX}{dx} = 4\pi\rho.$$

The variation of electric intensity with the distance is proportional to the amount of free electrification at the point (the number of ions per c.c.).

If we can determine experimentally the distribution of potential between the plates, or what is equivalent, the strength of the electric field at each point, we can calculate the distribution of the electrification.

Let us assume that the ions present are all of one sign and that the velocity of an ion is proportional to the strength of the field.

If u denote the velocity of an ion in unit field, then uX = velocity in field X .

Let n = number of ions in unit volume at any point. Then i the current at that point through unit area

$$= nuXe.$$

Also, since $\rho = ne$,

$$\frac{dX}{dx} = 4\pi ne.$$

Eliminating n we get

$$X \frac{dX}{dx} = \frac{4\pi i}{u}.$$

When a steady state is reached i is constant.

$$X^2 = X_0^2 + \frac{8\pi i}{u} x.$$

By means of this equation we can calculate the variation in the electric field due to the presence of negative ions between

the plates. The result of the calculation shows that the field is very nearly uniform.

Stoletow was unable to detect any want of uniformity experimentally.

Schweidler found a small variation in the strength of the field when the negative plate was illuminated, corresponding to an excess of negative ions at each point.

RELATION BETWEEN THE CURRENT AND THE STRENGTH OF THE ELECTRIC FIELD *

We have seen that the current per unit area flowing between two parallel metal plates is

$$i = nuXe.$$

The negative ions will be moving about in the space between the plates like the molecules of a gas. Some of them will strike against the negative plate and give up their negative charges to it. The number striking against unit area of the plate in unit time can be calculated if we assume that the ions are subject to the laws of the kinetic theory. On this assumption the number is found to be $cn/\sqrt{6\pi}$, where c is the average velocity of translation of the negative ions.

The steady state will be reached when the negative electricity given out by the plate in unit time is equal to the sum of the charge returned per unit time plus the current through the gas.

Thus
$$n_e e = \frac{cne}{\sqrt{6\pi}} + i,$$

where n_e is the number of electrons emitted from unit area in unit time.

But
$$ne = i/uX.$$

So
$$n_e e = \frac{ci}{\sqrt{6\pi}uX} + i,$$

or
$$i = \frac{n_e e \sqrt{6\pi}uX}{c + \sqrt{6\pi}uX},$$

an equation which determines the connection between the current through the gas and the electric field.

* J. J. Thomson, *Conduction of Electricity through Gases*, 2nd edition, pp. 267-268.

When X is small—that is, when uX , the velocity due to the field, is small compared with the mean velocity of translation of the ion—

$$i = n_0 e \sqrt{6\pi u X} e$$

and the current is proportional to the electro-motive force. But as X increases i increases less rapidly, and when X is large the current becomes approximately constant and equal to $n_0 e$, or a saturation value is reached.

The effect of variations of pressure on the current through the gas may be traced from the formula if we know how the ionic velocity depends upon the pressure. For moderate pressures the value of u was found to be inversely proportional to the pressure. For low pressures the results are complicated by the fact that ionisation by collision occurs for comparatively weak fields.

EXPERIMENTAL RESULTS AS TO THE VARIATION OF CURRENT WITH PRESSURE AND POTENTIAL DIFFERENCE

Measurements of the photo-electric current from a metal plate in air at various pressures were made by Stoletow.* The light from an arc lamp passed through a quartz plate silvered on the inner surface and ruled like a diffraction grating. It fell on a silvered plate whose distance from the grating could be adjusted by a micrometer screw. The current was measured by a very sensitive galvanometer.

At ordinary pressures the current approaches a kind of saturation as the potential difference is increased, provided the plates are only a small distance apart. The diagram (Fig. 15) shows the results of these experiments, the unit of potential difference being the electro-motive force of a Clark cell. The number $x+5$ attached to a curve indicates that the distance between the plates was $x+5$ mm., where x is a small distance, about 1.5 mm. From these results Stoletow inferred that the current i is the same at all distances d , provided E/d is the same—that is, $i = f(E/d)$, where E is the difference of potential between the plates. This relation no longer holds

* Stoletow, C. R., 108, p. 1241, 1889; *Journal de Physique*, ii., 9, pp. 468-473, 1890.

good when the pressure is reduced. For lower pressures there is no approach to saturation, but for still lower pressures saturation is again apparent.

Stoletow also examined the variation in the current with the pressure, keeping the potential difference constant. As the pressure was diminished, starting from atmospheric

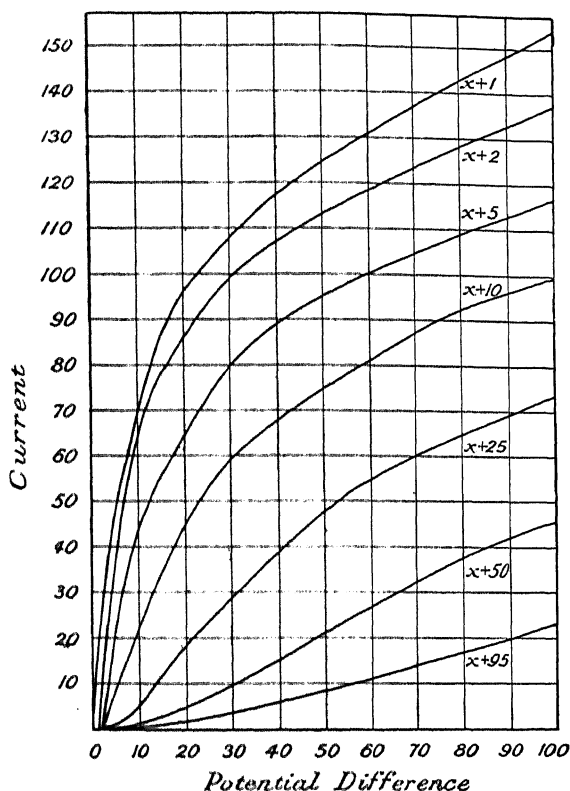


FIG. 15

pressure, the photo-electric current increased, at first very slowly, then more rapidly. At a certain definite pressure (the "critical pressure") the current reached a maximum value, and afterwards diminished towards a finite limit. The critical pressure p_m can be determined by the simple relation $p_m d/E = \text{a constant}$. If the pressure is in mm. of mercury, d in cm., and E in volts, the value of the constant is $1/372$.

The curves in the diagram (Fig. 16) illustrate the relation between the current and the pressure for three different values of the electric field, when the plates are .83 mm. apart. The Clark cell is again the unit of electro-motive force. At very low pressures the current is independent of the potential difference—*i.e.* it is saturated.

Experiments with a potassium cell prepared by the method of Elster and Geitel were carried out by E. v. Schweidler.* In discussing the relation between the current and the potential difference three stages may be considered. For potential

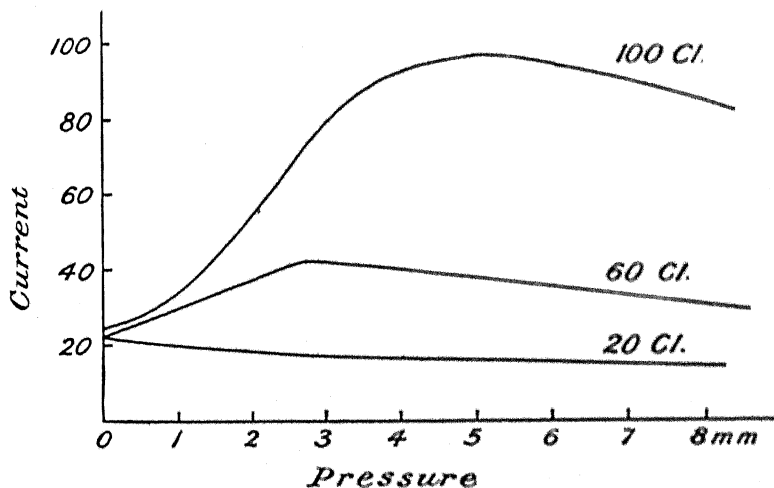


FIG. 16

differences up to about 2 volts the current is a linear function of the potential difference. From 2 volts up to about 70 volts the current increases more slowly, but cannot be said to approach saturation. When the potential difference exceeds 70 volts the increase in the current is much more rapid. On account of the fact that the intensity of illumination employed was not the same in the different series of experiments, we cannot illustrate these results by means of a single curve, but a typical curve of a similar character is given below (Fig. 17) from a later investigation of the same author.† In

* E. v. Schweidler, *Wien. Ber.*, **107**, pp. 881-909, 1898.

† *Ibid.*, **108**, pp. 273-279, 1899.

this research the current from an amalgamated zinc plate was measured for a wide range of potential differences, and for several different pressures. The curve reproduced corresponds to a pressure of about 17 mm.

A systematic examination of the dependence of the magnitude of the photo-electric current on the pressure and nature of the gas by which the illuminated surface is surrounded was made by Varley.* The method employed was to draw the

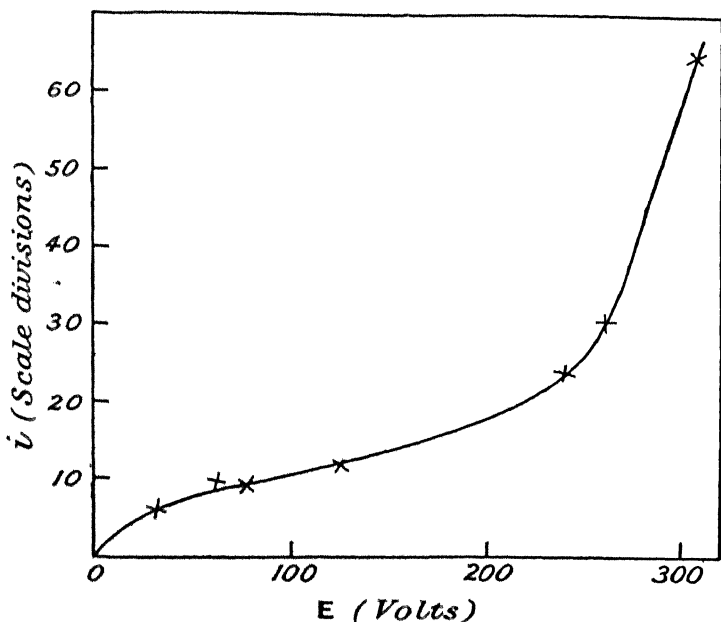


FIG. 17

complete curve connecting the current and the potential difference for each pressure, keeping the intensity of the illumination as constant as possible throughout the series of observations. An arc in hydrogen between iron wire terminals was used as the source of light, and the constancy of the source was tested by a separate apparatus, in which the conditions remained invariable.

The results obtained by varying the pressure of the gas are illustrated by the curves of Figs. 18 and 19, which refer

* Varley, *Phil. Trans. Roy. Soc., A*, 202, pp. 439-458, 1904.

to experiments with a zinc plate in hydrogen. The second figure is intended to show more clearly than the first the variation of the photo-electric current at very low pressures. Curves of similar character were obtained with a platinum kathode in air.

The conclusion of Stoletow—that when the potential is

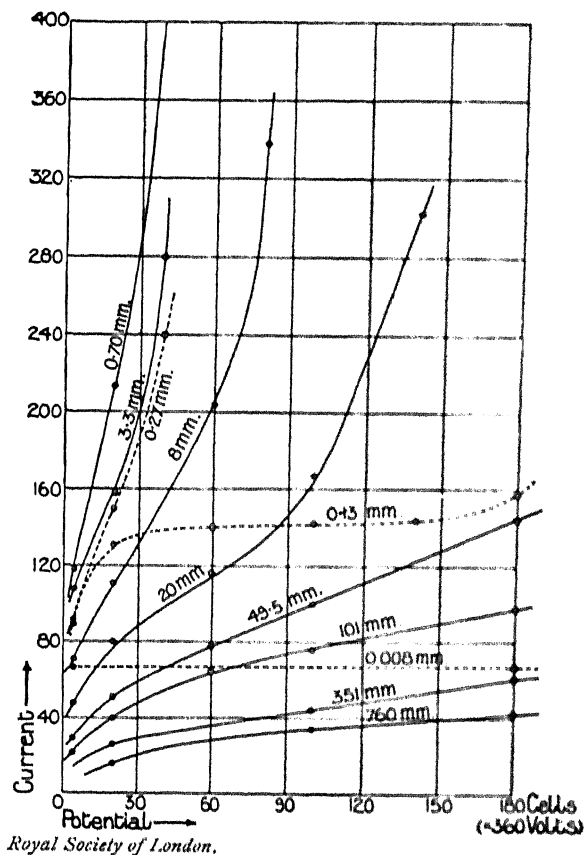


FIG. 18

kept constant and the pressure is gradually decreased, the current increases, reaches a maximum, and then diminishes towards a finite limit which is nearly independent of the potential—can be verified at once from Varley's curves in Fig. 18.

The results with regard to the variation of current with

potential difference may conveniently be described in three stages corresponding to the pressure at which the experiments are carried out. At ordinary pressures there exists a more or less flat part of the current-E.M.F. curve, corresponding to approximate saturation. As the pressure is lowered this flat part becomes steeper and steeper, until at a pressure of

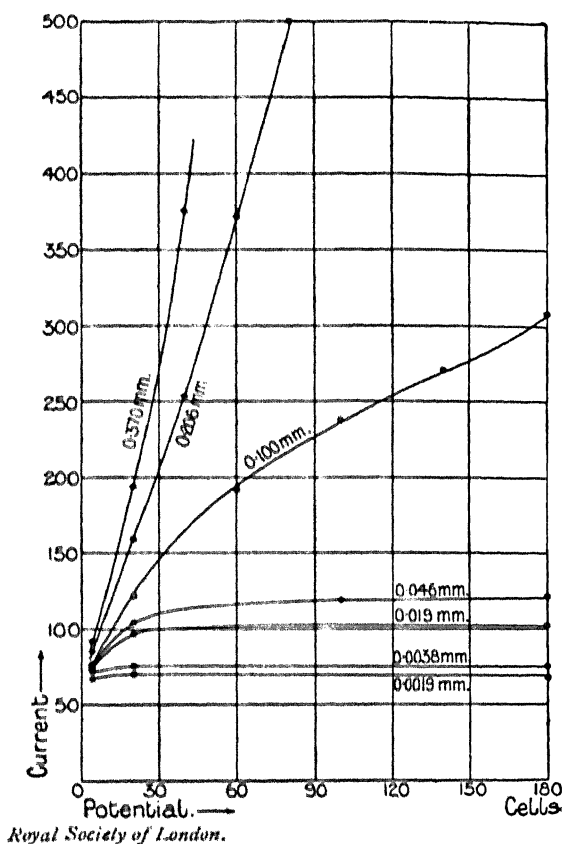


FIG. 19

a few millimetres there does not appear to be any approach to saturation. In this second stage a small change in the potential difference always produces a large alteration in the current. The third stage is only reached at much lower pressures, when we again get an approach to saturation. At a pressure of about a tenth of a millimetre, depending on the

distance between the electrodes, we get a true saturation current. This decreases with the pressure, and approaches a finite limit as the vacuum is made more nearly perfect.

In this third stage the mean free path of the ions becomes comparable with the distance between the electrodes. As soon as this is the case, the number of collisions which can

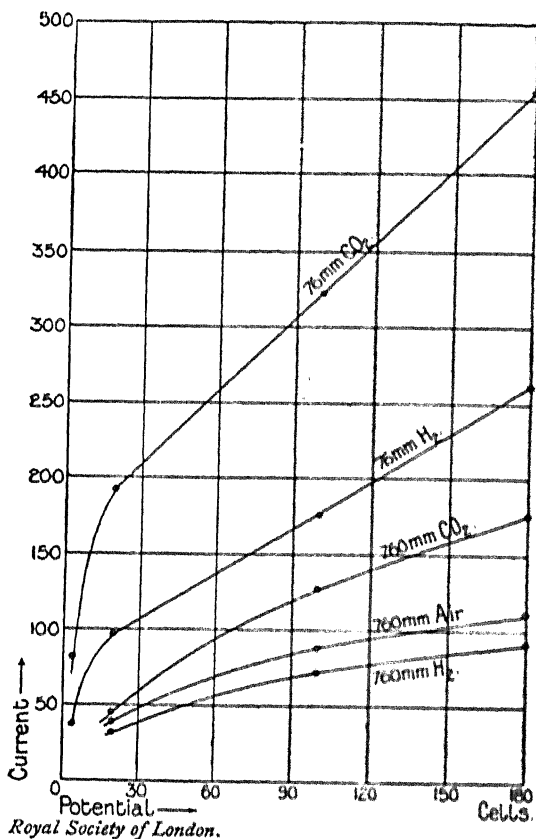


FIG. 20

occur between electrons shot off from the illuminated plate and gaseous molecules becomes very limited, and a small potential gradient is sufficient to cause saturation. At the very lowest pressures the curves agree with Lenard's result that a very large change in the potential difference produces no change in the current.

Experiments carried out in air, hydrogen, and carbon

dioxide by Varley yielded the following results (Figs. 20 and 21). At higher pressures the current is greater in carbon dioxide than in air, and greater again in air than in hydrogen, for all potential gradients up to those at which the genesis of ions by collision begins. The curves show that this stage begins in hydrogen at a much lower potential gradient than in air or carbon dioxide, the potential gradient required to cause ionisation by collision in these two gases being approximately

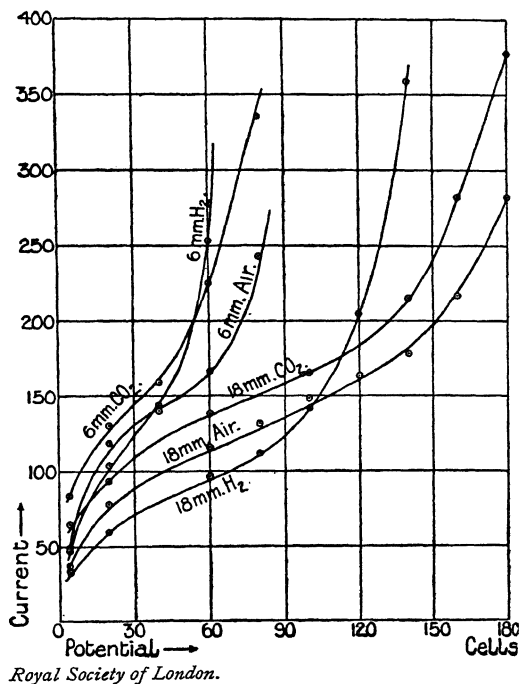


FIG. 21

the same. (The potential gradient necessary for a spark discharge to pass in hydrogen is only 0.55 times that required in air.)

Kreusler* in 1901 was the first to observe that all metals show a remarkably large photo-electric effect in the neighbourhood of the sparking potential. Experiments with zinc, iron, copper, silver, platinum, and aluminium all showed this increase in a marked degree (Fig. 22). This explains why the

* Kreusler, *Ann. d. Physik*, 6, p. 404, 1901.

material of the kathode in the experiments of Hertz had no

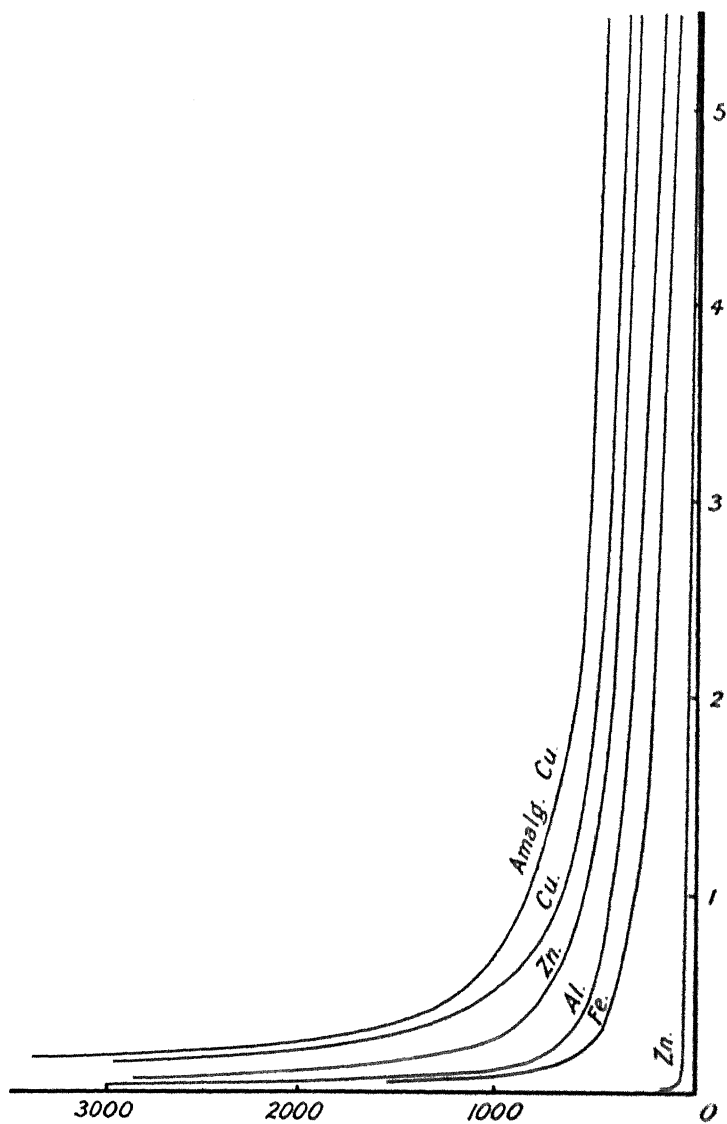


FIG. 22

The abscissa measured from O represents the difference between the potential applied and the sparking potential.

observable influence on the increase of spark length under the action of light.

The conductivity produced in gases by the motion of negatively charged ions has been investigated by J. S. Townsend,* who has collected his results in a book entitled *The Theory of Ionisation of Gases by Collision* (Constable and Co.). It is therefore unnecessary to do more than indicate briefly the principal conclusions arrived at. When the electric field is increased sufficiently, new ions are produced by collisions between ions and the molecules of the gas. At first this effect is due to negative ions alone, but when the sparking potential is approached the positive ions also produce fresh ions by collision.

Let X denote the electric force between two plates at a distance d apart, so that $X = (V_1 - V_2)/d$. Let p be the pressure of the gas. If one plate is illuminated by ultra-violet light, a certain number, n_0 , of negative ions will be set free. Suppose each ion in moving through 1 cm. of the gas produces a new negative ions, then a is a quantity depending on X , p , and the temperature. For small values of X , a is practically zero, unless p is also small. Let n be the number of ions produced within a distance x from the illuminated plate. Then in going a distance dx these will produce $andx$ new ions.

$$\text{Thus } dn = andx,$$

$$\text{and therefore } n = n_0 e^{ax}.$$

The total number of ions reaching the positive plate will be $n = n_0 e^{ad}$.

For different distances between the two plates we have $n_1 = n_0 e^{ad_1}$, $n_2 = n_0 e^{ad_2}$, $n_3 = n_0 e^{ad_3}$.

$$\text{Therefore } \frac{n_2}{n_1} = e^{a(d_2 - d_1)}, \quad \frac{n_3}{n_2} = e^{a(d_3 - d_2)}.$$

If we choose the distances between the plates so that $d_2 - d_1 = d_3 - d_2$, we get $\frac{n_2}{n_1} = \frac{n_3}{n_2}$.

This relation was verified by Townsend for air, hydrogen, and carbonic acid at a number of different pressures. The values of a can be determined from the results of such experiments.

* J. S. Townsend, *Nature*, **62**, p. 340, August 9, 1900.

This coefficient α , the number of ions of one kind that a single negative ion will generate in moving under an electric field through a centimetre of the gas, depends, when the temperature is constant, on the strength of the field and the pressure. Townsend * showed, both by theory and experiment, that it satisfies the relation

$$\frac{\alpha}{p} = f\left(\frac{X}{p}\right)$$

By assuming that one pair of ions is formed when the velocity at collision exceeds a certain value, and that after a collision a negative ion practically starts from rest along its new path, Townsend obtains the relation

$$\frac{\alpha}{p} = N e^{-\frac{NVp}{X}}$$

In this equation N , the maximum value of α , is the number of collisions that an ion makes in travelling through a distance of 1 cm. in a gas at 1 mm. pressure, and V is the potential difference between the ends of a path along which an ion acquires sufficient velocity to generate others by collisions.

The values of N and V found from the observations are as follows :

	Air	N ₂	H ₂	CO ₂	HCl	H ₂ O	A	He
N	14.6	12.4	5.0	20.0	22.2	12.9	13.6	2.4
V	25	27.6	26.0	23.3	16.5	22.4	17.3	14.5
NV	365	342	130	466	366	289	235	34.8

Since $n = n_0 e^{ad}$, the photo-electric current is given by the formula

$$i = i_0 e^{d \left(\frac{\alpha}{p} N e^{-\frac{NVap}{E}} \right)}$$

where i_0 is the current in the highest vacuum and the field strength X is given by E/d . The maximum value of the current corresponds to a pressure p_m determined by

$$\frac{E}{dp_m} = NV = \text{const.}$$

This is the relation given by Stoletow, and the value of the constant obtained by him is in good agreement with the value of NV determined from Townsend's experiments.

* Townsend, *Phil. Mag.*, 1, p. 637, 1901.

The maximum current i_m is given by the equation

$$i_m = i_0 \epsilon^{X/V\epsilon}.$$

A modification of Townsend's formulæ has been suggested by Partzsch.* Instead of taking into account the whole distance d between the plates in considering the effect of ionisation by collision, only the fraction $d(1 - \frac{V}{E})$ is supposed effective. The principal formulæ then become

$$n = n_0 \epsilon^{ad(1 - \frac{V}{E})},$$

$$i = i_0 \epsilon^{d(1 - \frac{V}{E})\rho N\epsilon - \frac{NV\rho d}{E}},$$

$$i_m = i_0 \epsilon^{\frac{E-V}{E\epsilon}},$$

while Stoletow's relation,

$$\frac{E}{d\rho_m} = NV,$$

remains unchanged.

Experiments carried out in air, nitrogen, oxygen, and hydrogen show good agreement between the observed values of the current and those calculated by means of the proposed formula. This is illustrated in the case of air by the curve of Fig. 23, where the circles indicate the observed, the dots the calculated values.

The values of the constants are given in the following table, which also gives the values of L , the free path of a gas molecule at 1 mm. pressure, and of $\frac{I}{N}$ the mean free path of an ion under the same conditions.

	NV	V	N	I/N(cm.)	L	I/N:L
Air . .	340	27.1	12.6	.0794	.00745	10.65
Nitrogen .	346	27.9	12.4	.0807	.00734	11.00
Hydrogen .	153	27.8	5.5	.182	.01375	13.22
Oxygen .	268	23.9	11.2	.0893	.00794	11.25
Carbonic acid	380	23.5	16.2	.0618	.00512	12.07

It appears that the free path of an ion is about eleven times as large as the free path of a molecule, and consequently

* Partzsch, *Verh. Deutsch. Phys. Gesell.*, 14, pp. 60-73, 1912.

about twice as great as that of a vanishingly small particle in rapid motion.*

In dealing with the photo-electric discharge in different gases there are several points that have to be considered, besides the values of the constants V and N . If the field between the plates is sufficiently strong, it is necessary to

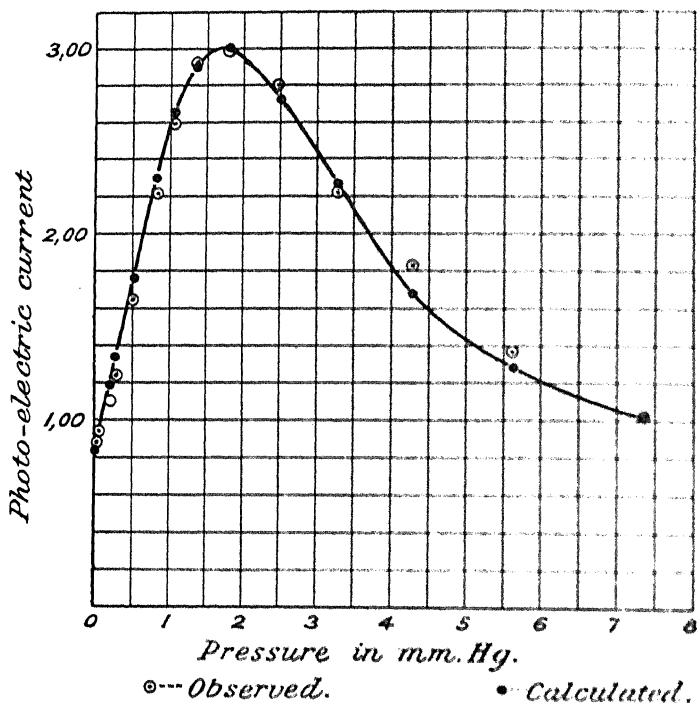


FIG. 23

take into account the effects due to the motion of positive ions. Townsend has shown that the positive ions produce others by collision when the potential between the plates is large, but still much less than that required to produce a spark.

Assuming the theory already sketched as to the production of ions in the gas by adhesion or collision, we still have to face the problem of determining whether the number of elec-

* J. C. Maxwell, *Phil. Mag.* (4), **19**, p. 29, 1860.

trons emitted from the surface is affected by the nature of the surrounding medium. We can imagine that the number might be altered by the condensation of gas in the pores of the plate, or by the formation of a surface film. There is also the possibility of a change in the character of the surface in consequence of chemical action between it and the gas. Thus a trace of the vapour of bromine or iodine is sufficient to destroy the sensitiveness of a zinc plate.

The effect of the surrounding medium on photo-electric activity has been examined by T. Wulf.* He found a considerable increase in the activity of a platinum plate when air was replaced by hydrogen. Platinum "polarised" by hydrogen becomes very active. He concluded that the discharging power becomes greater as the electro-chemical difference of potential between the plate and the medium in which it is immersed is made greater. Thus, with a newly polished platinum plate the discharge is in the order—hydrogen, oxygen, chlorine, ozone. Experiments with zinc and silver plates gave similar results.

The effect of surface films in altering the activity of a metal plate will be discussed later in connection with the subject of photo-electric fatigue.

* Wulf, *Ann. der Physik*, 9, pp. 946-963, 1902.

CHAPTER VI

PHOTO-ELECTRIC SUBSTANCES: SOLIDS AND LIQUIDS

THE characteristic feature of photo-electric action is the loss of a negative charge, or the acquisition of a positive charge, under the influence of light. This is traced to the emission of negative electrons from the illuminated surface. It is of great importance to know how various substances compare with one another in regard to such emission, and to see if any relations can be traced between the photo-electric activity and the other properties of the substances examined.

In order to compare the photo-electric activity of different materials, the tests must be carried out under corresponding conditions. This is a matter of some difficulty, especially as it is not easy to determine in the first instance what conditions are to be regarded as "corresponding." The activity varies in a marked degree with the character and intensity of the light employed, so that a comparison of various substances under the influence of a particular source of light would probably yield results differing from those obtained with some other source.* For an exact scientific study of the subject experiments are required with mono-chromatic light of known frequency and intensity. Further, unless the experiments are made in a good vacuum the activity depends on the temperature. Again, the photo-electric current through a gas depends on the electro-motive force applied, and, strictly speaking, a "saturation" current is never obtained when the test is made in a gas. Consequently the only satisfactory plan would be to compare the substances in a very good vacuum, when, as Lenard has shown, the discharge is independent of the potential difference for a wide range of values of the latter.

* Eugène Bloch, *Le Radium*, 7, May 1910.

Even when this plan is adopted the results obtained depend, as a rule, on the condition of the illuminated surface. It is not surprising, therefore, that comparatively little progress has been made up to the present in establishing relations between the photo-electric properties of a substance and its physical or chemical constitution. On this account it is difficult in the present chapter to do more than summarise the principal measurements that have been made in connection with the photo-electric activity of various substances. We deal first with the metals, then with a number of compounds of the metals, and finally with certain non-metallic compounds, including a number of organic dyes and some insulating materials.

A short discussion follows, dealing with certain phenomena more or less closely related with the photo-electric effect, such as the electro-motive force set up in the light-cells of Becquerel and Minchin, and the variation in the electrical resistance of certain substances caused by illumination.

The results obtained in connection with the very important subject of the photo-electric activity of gases and vapours are reserved for a separate chapter.

PHOTO-ELECTRIC ACTIVITY OF METALS

The great difficulty met with in attempting to classify the metals in the order of their photo-electric power is due to the remarkable variations in the activity under different experimental conditions. The method of preparing the metal surface gives rise to differences that are often very large. Many observers have thought that the photo-electric activity increased with the degree of polish of the surface. On the other hand, Hallwachs* found that a copper plate first polished with fine emery-paper showed almost the same activity after it had been rubbed with very coarse emery.

Ullmann† showed that the values obtained by filing the surface of a metal were far more constant than those obtained

* Hallwachs, *Ann. d. Physik*, **28**, p. 465, 1907.

† Ullmann, *Ann. d. Physik*, **32**, p. 1, 1910.

by the use of emery-paper. H. S. Allen * examined the photo-electric behaviour of dry iron in the active and passive state, and found that when the iron is chemically active it exhibits large photo-electric activity, while in the passive state this activity is greatly diminished.

Further, we have to take into account the variation in the activity with the age of the surface, frequently observed when the metal is tested in a gas. The activity generally diminishes, at first rapidly, then more slowly, owing to changes in the condition of the gaseous layer at the surface or to other causes that are discussed in the chapter on photo-electric fatigue.

The most satisfactory method of preparing a metal surface that shall be perfectly pure and free from surface films is that devised by Hughes, in which the material is obtained by distillation in a very high vacuum. The process is described in Chapter X.

The first experiments on the loss of a negative charge by an illuminated surface were carried out with metals. Hallwachs mentions that he found iron less active than zinc, and zinc less active than aluminium. Elster and Geitel † investigated the photo-electric properties of a large number of substances. Zinc and aluminium give a measurable effect in sunlight, but copper, platinum, lead, iron, cadmium, carbon, and mercury require light richer in ultra-violet rays. The more electro-positive metals are specially active, and lose a negative charge in ordinary daylight. Elster and Geitel experimented with amalgams of sodium and potassium, and also with the metals themselves. The liquid alloy of sodium and potassium can be manipulated with greater ease than the solid metals. A convenient method of preparing an experimental tube containing the alloy has been described by Fleming.‡ Elster and Geitel give the following list to represent the order of the photo-electric effect of the metals: rubidium, potassium,

* H. S. Allen, *Proc. Roy. Soc., A*, **88**, pp. 70-74, 1913.

† Elster and Geitel give a summary of their results in *Nature*, **50**, p. 451, 1894.

‡ Fleming, *Phil. Mag.*, **17**, pp. 286-295, 1909.

alloy of potassium and sodium, lithium, magnesium, thallium, zinc. The order in this list, and, generally speaking, the order for the more electronegative metals *tested in air*, is the same as the order in the voltaic series for contact potential. The more electropositive a metal the greater is its photo-electric activity.

Attempts to classify the metals have been made by various experimenters. Ramsay and Spencer,* and also Herrmann,† made tests in air at atmospheric pressure. The former arrange the metals in the following order: Al, Mg, Zn, Sn, Cd, Pb, Bi, Au, Ni, Co, Cu, Ag, Fe. This list was obtained with metal surfaces polished as well as possible, using a mercury vapour lamp of Uviol-glass as the source of light. In the experiments of Herrmann each metal was polished so as to obtain the maximum effect, the source of light in this case being a carbon arc lamp. The order given is Al, Zn, Mg, Sn, Bi, Cd, Pb, Cu, Ni, Co, Ag, Au, Fe. Although such lists can have no great scientific value, they are included in order to show that the order in air is roughly parallel to that of the Volta contact series.

The results obtained by the earlier experimenters who worked in vacuum are remarkable for the wide divergencies shown. The order of the metals in these lists bears no relation to the order at atmospheric pressure, or to the Volta contact series. E. Ladenburg gives the order Cu, Brass, Zn, Bi, Pt, Ni, Fe, Au, Ag; Millikan and Winchester give Cu, Au, Ni, Brass, Ag, Fe, Al, Mg, Sb, Zn, Pb. In Ladenburg's experiments‡ the surface was first polished with emery and oil, and finally with chalk applied with a clean linen rag. The tube containing the metal under test was exhausted till the discharge of a large induction coil would no longer pass through it. A spark between aluminium electrodes served as a source of ultra-violet light. Millikan and Winchester§ were careful to avoid the use of

* Ramsay and Spencer, *Phil. Mag.*, **12**, p. 397, 1906.

† Herrmann, *Beiträge zum Hallwacheffekt*, Diss. Berlin, 1908.

‡ E. Ladenburg, *Ann. d. Physik*, **12**, pp. 558-578, 1903.

§ Millikan and Winchester, *Phil. Mag.*, **14**, pp. 188-212, 1907.

oil in preparing the surfaces. The metals were cleaned but not polished. The experiments were carried out in a good vacuum, the source of light being a spark discharge between zinc electrodes. In spite of the precautions taken by these investigators, their results cannot be accepted as showing the true relative values of the activity, since recent experiments have shown that the only satisfactory way of securing a perfectly clean metal surface is by preparing it in vacuo.

Incidentally we may notice that Millikan and Winchester also measured the positive potential assumed by the metals in a vacuum under the influence of ultra-violet light. The order in this list differs from the order of the photo-electric sensitiveness, and bears no relation to the Volta contact series.

Metal.	Positive Potential in Volts at 26° C.	Rate of Discharge at 25° C.
Ag . . .	1.340	17.16
Fe . . .	1.225	16.40
Au . . .	1.215	24.70
Brass . . .	1.174	23.80
Cu . . .	1.135	25.10
Ni . . .	1.126	24.00
Mg839	11.00
Al738	14.90
Sb394	4.00
Zn197	1.20
Pb0	0.90

The positive potential may be taken as a measure of the velocity of emission of the electrons. The question of the velocity of emission from different metals will be considered at length in connection with the influence of the wave-length of the exciting light on photo-electric phenomena (Chapter X). Einstein's unitary theory of light points to the conclusion that an electron can only escape from a metal when the energy of a light unit is at least equal to V_e , the work that must be done in carrying the electron (charge e) through the potential difference between the metal and the gas. The theory of

photo-electric emission developed by Richardson leads to a similar result, for he finds expressions for the number of electrons emitted and the energy of emission which contain a term dependent on the contact difference of potential (Chapter XI). These formulæ are in agreement with the recent experimental investigations of Richardson and Compton, and of Hughes.

The contact difference of potential, as Erskine Murray has shown, varies greatly with the state of the metal surface as regards polish and the presence of gaseous films. The photo-electric sensitiveness is also largely affected by such surface conditions. Before any definite conclusions can be drawn as to relations between the two sets of phenomena, it is desirable to have simultaneous measurements of both effects. Such measurements have been made by Hallwachs,* Ullmann,† and Compton.‡ The results prove that though it is necessary to take into account the contact difference of potential in estimating the electric field acting upon the electrons, this difference of potential is not responsible for the large variations actually observed in the strength of the photo-electric current. Surface films may produce large changes in the strength of the current if their constitution is such that they are strong absorbers of the effective radiations (Chapter XII).

H. Dember§ has carried out experiments to determine whether any connection can be established between the photo-electric effect and the kathode fall of potential with an alkali electrode in various gases. A relation exists between the kathode fall of potential and the position of the metal in the Voltaic series. If the photo-electric current is due to the emission of negative electrons from the illuminated kathode, a connection between the photo-electric activity and the kathode fall of potential would appear probable. A large light effect is to be expected where the smallest kathode fall of potential is to be found. According to this hypothesis

* Hallwachs, *Ann. d. Physik*, **23**, p. 481, 1907; *Deutsch. Phys. Gesell. Verh.*, **14**, p. 638, 1912.

† Ullmann, *Ann. d. Physik*, **32**, p. 46, 1910.

‡ Compton, *Phil. Mag.*, **23**, pp. 579-593, 1912.

§ H. Dember, *Annalen der Physik*, **20**, p. 379, 1906.

the photo-electric activity of the alkali metals should be large, and larger in helium than in hydrogen. This was found to be the case for sodium-potassium alloy both for ultra-violet and for visible light. The kathode fall for the alloy in argon is smaller than for the same substance in helium. For higher voltages the photo-electric activity of the alloy is greater in argon than in helium.

For some purposes it is important to secure a photo-electric cell which shall have as great sensitiveness as possible. The sensitiveness of a cell containing one of the alkali metals in an atmosphere of hydrogen at low pressure may be considerably increased, as Elster and Geitel* have shown, by the formation of a so-called alkali-hydride and by passing a glow discharge through the tube. If the hydrogen is then replaced by helium, the cell is rendered more permanent and can be used for photometry. J. G. Kemp† has studied the conditions necessary to secure maximum sensitiveness for a potassium cell in an atmosphere of hydrogen. The cell is about 100 times more sensitive after the formation of the hydride than before. The distance between the electrodes should be about 0.5 cm., the pressure of the hydrogen gas between 2 and 3 mm. of mercury, the temperature about 25° C., and the potential difference applied to the electrodes about 330 volts. With such a cell, used in connection with a tilted electroscope capable of measuring a current of 10^{-15} amperes, the author calculates that it would be possible to detect a candle at a distance of 2.7 miles.

A sensitive photo-electric cell, in which the inside of a pear-shaped flask is coated with a layer of distilled sodium, has been described by Hughes.‡ The flask is provided with a quartz window, through which the ultra-violet light enters. By an ingenious device the deposition of sodium on this window is prevented. Using light of wave-length $436 \mu\mu$ isolated by a monochromator from a mercury lamp absorbing

* Elster and Geitel, *Phys. Zeitschr.*, **11**, pp. 257-262, 1910; **12**, pp. 609-614, 1911.

† J. G. Kemp, *Phys. Rev.* (2), **1**, pp. 274-293, 1913.

‡ Hughes, *Phil. Mag.*, **25**, pp. 679-682, 1913.

120 watts, the current obtained was as large as 580×10^{-11} amperes.

PHOTO-ELECTRIC ACTIVITY OF METALLIC COMPOUNDS

Most of the experiments on compounds of the metals have been carried out in air at atmospheric pressure. The results are very greatly influenced by the condition of the surface and the character of the light employed. Further results are much to be desired with the employment of monochromatic ultra-violet light and with a surface prepared by the distillation of the compound in a high vacuum, as in the experiments of Hughes.

Generally speaking, the compounds of the metals with sulphur or the halogens show the greatest photo-electric activity. It is significant that these compounds are those which frequently show marked phosphorescent effects; thus Balmain's luminous paint is photo-electrically active.

G. C. Schmidt* measured the photo-electric activity of a number of solid substances, using an electrometer (1 volt = 150 scale divisions) and noting the deflection after three minutes' illumination. Very large effects were observed in the case of the sulphides of copper and chromium, and a large effect was found for sulphide of bismuth. The chloride, bromide, and iodide of silver all gave about the same large deflection. Smaller deflections were obtained from iron sulphide, zinc sulphide, zinc sulphate, zinc oxide, mercury chloride, and copper iodide. A large number of substances, including the haloid salts of the alkali metals, showed no activity when tested by this method. It is remarkable that most of the substances examined showed strong action when tested in contact with the negative terminal of a spark-gap by the method of Hertz, even though they showed no photo-electric activity when the difference of potential was 560 volts.

The activity of a number of metallic salts was measured by O. Knoblauch,† who found large activity in the case of the sulphides of lead, manganese, and mercury, smaller activity

* G. C. Schmidt, *Wied. Ann. d. Physik*, **64**, p. 708, 1898.

† O. Knoblauch, *Zeit. Phys. Chem.*, **29**, p. 527, 1899.

for sulphide of tin and trisulphide of antimony and of arsenic. Bromide of copper was fairly active, the chloride less so. Both the oxides of copper were moderately active. Amongst substances which gave only a small effect were silver oxide, mercury iodide, and cadmium sulphide.

A detailed examination of the metal sulphides was made by Rohde,* who found that in general they showed considerable photo-electric activity. This activity was dependent in a marked degree on the condition of the surface—especially the roughness—on the density, and on the molecular structure (*e.g.* crystalline form). Most of the sulphides were tested in the form of mineral, of powder, and of pastilles prepared with the hydraulic press. In general the mineral showed the greatest, the powder the least activity. The metals may be roughly arranged in the order of diminishing activity as follows: lead, copper, manganese, silver, tin, iron, chromium, bismuth, nickel, antimony, zinc, cadmium, cobalt, and molybdenum. In the case of lead glance (PbS) the activity in the form of mineral, powder, and pastille is represented by the numbers 887, 602, and 874 respectively. Under the same experimental conditions a clean zinc plate would have an activity of 530, and an aluminium plate of about 200. In these experiments the extreme ultra-violet rays from a spark between zinc terminals were employed. When examined under these conditions the sulphides in most cases show greater activity than the metals themselves. When tested with the light of a Nernst lamp, they show much less activity than the metals. This has been confirmed by Herrmann,† who found that Uviol glass cut off most of the radiation effective with the metal sulphides.

The sulphides of certain metals have been examined by Ramsay and Spencer,‡ who recorded the time taken for the gold leaf of their electroscope to pass over ten scale divisions when the substance under test was illuminated. The sulphides in one series of experiments were prepared by placing the metal in either a solution of sulphuretted hydrogen or one of

* Rohde, *Annalen d. Physik*, **19**, pp. 935–959. 1906.

† Herrmann, *Beiträge zum Hallwacheffekt*. Diss. Berlin, 1908.

‡ Ramsay and Spencer, *Phil. Mag.*, **12**, p. 397. 1906.

ammonium sulphide; in a second series the precipitated sulphide was made into a paste with starch solution and dried upon the plates. The activity obtained by the second method was, as a rule, smaller than that obtained by the first. The sulphides of copper and lead were the most active of those examined, their activity being about 30 and 25 per cent. respectively of that of a clean copper plate. The activity for the sulphides of antimony, iron, tin, and cadmium only amounted to 2 or 3 per cent. According to these results the sulphides are much less active than the pure metals. This no doubt depends upon the source of light employed (in these experiments a mercury arc in Uviol glass).

The iodides of the five metals copper, silver, cadmium, tin, and lead, were prepared by suspending plates of the metals over a dish of iodine until the surface was coated with the salt. The activity was found to be according to the order named, iodide of copper, which gave the greatest effect, showing an activity of about 8 per cent. as compared with metallic copper. With the exception of silver iodide, the only moniodide in the series, the activity diminishes with increasing percentage of iodine in the salt.

The photo-electric activity of the halogen compounds of copper, illuminated by the light from a carbon arc, has been measured by Pochettino,* who also determined for these compounds the order of the Becquerel effect, that is the increase in electro-motive force due to illumination of an electrode. The two effects appear to be connected, but the order of sensibility is not the same in the two cases. This is shown in the following table, where the more active substance stands earlier in the series :

Photo-electric effect. (Activity).	Becquerel effect.
CuI_2^\dagger . . . 39	CuBr_2
CuBr_2 . . . 32	CuI_2
CuCe_3 . . . 20	CuO
$\left\{ \begin{array}{l} \text{CuO} \\ \text{CuF}_2 \end{array} \right.$. . . 3	$\left\{ \begin{array}{l} \text{CuCl}_2 \\ \text{CuF}_2 \end{array} \right.$

* Pochettino, *Accad. Lincei, Atti*, 16 (2), pp. 58-66, 1907.

† The sensibility of the copper iodide was compared directly with that of amalgamated zinc, and the ratio found to be 39 : 6.

Light of short wave-length is more effective as regards the first effect, while light of longer wave-length produces greater change in the second case.

My interest in photo-electric phenomena was first aroused whilst working in Lord Blythswood's laboratory at Renfrew in 1904, by noticing that freshly ground fluor-spar caused a considerable leak of negative electricity, the amount of leak falling off in the course of a few minutes after grinding. The effect took place in ordinary daylight after traversing two thicknesses of glass, but no effect could be observed in the dark.

Elster and Geitel* had already recorded the photo-electric activity of fluor-spar and other phosphorescent minerals. Different specimens of fluor-spar vary considerably in activity. The effect may perhaps be due to traces of the more electro-positive metals scattered through the substance of the spar, and imparting to it its colour.

According to Elster and Geitel, ultra-violet light is *not* the most efficient in this case. This suggests the presence of a selective photo-electric effect, such as is found with the metals of the alkali and alkaline earth groups.

Goldstein† discovered that certain salts, especially the alkaline haloids, become coloured when exposed to the kathode rays; at the same time their phosphorescence diminishes. The colours fade away, slowly in darkness but more rapidly in daylight, especially if the temperature is raised. Elster and Geitel‡ have shown that the salts thus modified exhibit marked photo-electric activity. This property gradually diminishes, and disappears at the same time as the coloration. Certain glasses acquire the photo-electric property under the influence of the kathode rays. In these cases also the activity may be due to traces of metal liberated by the action of the kathode rays.

The most important experiments on the activity of metallic compounds that have been carried out in a high vacuum up to the present time are those of W. Wilson and A. I. Hughes.

* Elster and Geitel, *Wied. Ann. d. Physik*, **44**, p. 722, 1891.

† Goldstein, *Wied. Ann. d. Physik*, **54**, p. 371, 1895; **55**, p. 491, 1897.

‡ Elster and Geitel, *Wied. Ann. d. Physik*, **59**, p. 487, 1896.

In the experiments of W. Wilson * peroxide of lead was used as a standard substance ; this has the same activity as aluminium, but shows little fatigue. Silver iodide, illuminated by ultra-violet light from an arc lamp, showed an activity 10.9 times that of the standard. A silver plate under the same illumination had an activity 3.56 times that of the standard. When the silver iodide was illuminated with violet light no photo-electric current could be detected. A layer of silver iodide on platinum was saturated with calcium nitrate solution. The material so treated still showed no activity with violet light, but with ultra-violet the activity was increased to about 54 times that of the standard. The photo-electric activity of silver sulphide was also measured, and found to be 9.5 times that of the standard.

Interesting results have been obtained by Hughes † from experiments in vacuo on certain solid compounds. In most cases the surface was prepared by distillation of the salt in a high vacuum. ZnCl_2 and P_2O_5 show no photo-electric effect when dry, but after contact with moist air they show distinct activity. There is practically no effect for FeCl_3 , and only a very small one for PbI_2 , after exposure to ultra-violet light. The other halogen salts (HgI_2 , HgI , HgCl , HgCl_2 , BiCl_3) show marked activity after they have been exposed to ultra-violet light. The initial effect in these cases is either zero or very small, but exposure to light increases the magnitude of the action. SbI_3 differs from the other salts in that a large leak is observed at the outset, and this is reduced by prolonged exposure. It is suggested that the halogen salts themselves are not photo-electric with wave-lengths longer than $184.9 \mu\mu$, but that the light first of all decomposes the compound and then acts on the metal in the ordinary way. It is difficult to reconcile the behaviour of SbI_3 with this explanation.

* W. Wilson, *Ann. d. Physik*, **23**, pp. 107-130, 1907.

† Hughes, *Phil. Mag.*, **24**, pp. 380-390, 1912.

PHOTO-ELECTRIC ACTIVITY OF NON-METALLIC COMPOUNDS

Bichat and Blondlot,* employing the method devised by Stoletow, find that water shows no photo-electric current when illuminated by light from the arc. A sheet of water is perfectly transparent to much of the effective radiation. Kreusler † found that pure water transmitted ultra-violet light to wave-length $200\ \mu\mu$, but absorbed light of shorter wave-length. Soapy water or a solution of calcium chloride may be used to cover the surfaces of bodies in order to prevent any photo-electric discharge from taking place. Certain impurities, however, tend to confer photo-electric activity upon water, and, according to Bloch,‡ it is extremely difficult to secure pure water which will show no trace of such activity. The subject has recently been investigated afresh by Hughes,§ who finds a very small irregular leak from a water surface, which he attributes to some spurious effect, such as the action of stray light or traces of impurity.

The activity of many of the aniline dyes was noticed soon after the discovery of the photo-electric effect. Stoletow || observed a discharge from solution of eosin, fluorescein in ammonia, fuchsin, and aniline violet, and in a later paper refers to the extreme sensibility of fuchsin and aniline green and violet, whether in the solid state or in solution. Hallwachs ¶ observed the activity of solutions in water of fuchsin, cyanin, iodine green, also of potassium nitrate, formic acid, and aniline.

G. C. Schmidt ** also made experiments on the aniline dyes eosin, fuchsin, methyl-violet, malachite-green, and magdalar-red. In the solid state these all showed photo-electric activity. In solution the results were difficult to interpret :

* Bichat and Blondlot, *C. R.*, **106**, p. 1349, 1888.

† Kreusler, *Ann. d. Physik*, **6**, pp. 412-423, 1901.

‡ E. Bloch, *C. R.*, **148**, pp. 621-622, 1909.

§ Hughes, *Phil. Mag.*, **24**, pp. 380-390, 1912.

|| Stoletow, *C. R.*, **106**, p. 1593, 1888 ; **108**, pp. 1241-1243, 1889.

¶ Hallwachs, *Wied. Ann. d. Physik*, **37**, p. 666, 1889.

** G. C. Schmidt, *Wied. Ann. der Physik*, **64**, p. 708, 1898.

Solvent.	Fuchsin (1/1000 normal).	Methyl-violet (saturated).
Water	219	240
Alcohol	17	157
Amylalcohol	0	175
Acetone	5	83

Fuchsin and methyl-violet are not very different in chemical constitution, yet there are marked differences in the photo-electric activities in the table. Malachite-green showed activity in all four solvents; magdala-red showed activity in solution in alcohol and amylalcohol, but not in acetone. Eosin, though not strongly active, shows some effect in all four solvents.

O. Knoblauch* has published a lengthy list showing the photo-electric discharge from various organic substances, including a large number of aniline dyes.

Solid surface films are formed on aqueous solutions of various organic dyes. These films gradually increase in strength up to a definite limit. Rohde† has shown that in the case of fuchsin and methyl-violet the film manifests photo-electric activity, which also increases up to a limit. This has been confirmed by Plogmeier,‡ who showed that the phenomenon is not due to an oxidation process. Inorganic colloids, like arsenic and antimony trisulphides, exhibit similar behaviour. The formation of a surface film does not always proceed parallel with the photo-electric effect.

A large number of organic substances, mostly derivatives of benzene, have been examined by Stark and Steubing,§ with a view to testing Stark's theory of the absorption of light by these compounds. The investigators come to the conclusion

* O. Knoblauch, *Zeit. Phys. Chem.*, **29**, p. 527, 1899.

† Rohde, *Ann. d. Physik*, **19**, pp. 935-959, 1906.

‡ Plogmeier, *Deutsch. Phys. Gesell. Verh.*, **11**, pp. 382-396, 1909.

§ Stark and Steubing, *Phys. Zeit.*, **9**, pp. 481, 661, 1908.

that the absorption of light in absorption bands shaded towards the red is accompanied by a photo-electric effect and also by fluorescence. (See Chapter XIII.)

The photo-electric properties of anthracene (Chapter XIV, p. 202) have been the subject of a number of investigations.* Pochettino showed that the photo-electric effect is of the same order as that of zinc, being greater for the fused than for the crystalline substance. Unless the material is in very thin layers the activity diminishes with the time. This is attributed to the high insulating power of the solid, which permits the accumulation of a positive charge upon the surface. Stark and Steubing found photo-electric activity not only with solid anthracene but also with anthracene vapour. Byk and Borck confirmed the result that the solid shows a real photo-electric activity, special precautions being taken to guard against errors due to the fact that the substance is a good insulator. Hughes made experiments with anthracene in a high vacuum, and found that it was only active for wavelengths shorter than $200.2 \mu\mu$.

The photo-electric properties of insulating materials have been investigated by R. Reiger.† Almost all such bodies lose a negative charge when exposed to the light of an electric arc. The material to be tested was in the form of a square plate of side 6 cm. On the back of the plate was a circular disk of tinfoil of diameter 4 cm., in metallic connection with the negative terminal of a battery giving 2400 volts. The negative charge from the illuminated front surface was received by a parallel metal plate connected to one set of quadrants of an electrometer. The following results were obtained, using the light from an arc lamp.

* A. Pochettino, *Atti dei Lincei* (5), **15** (1), pp. 355-363; **15** (2), pp. 171-179, 1906. Stark and Steubing, *Phys. Zeit.*, **9**, pp. 481, 661, 1908. Byk and Borck, *Deutsch. Phys. Gesell. Verh.*, **12**, pp. 621-651, 1910. Steubing, *Deutsch. Phys. Gesell. Verh.*, **12**, pp. 867-868, 1910. L. S. Stevenson, *Journ. Phys. Chem.*, **15**, pp. 843-865, 1911. Hughes, *Phil. Mag.*, **24**, pp. 380-390, 1912.

† R. Reiger, *Ann. d. Physik*, **17**, p. 935, 1905.

Insulator.	Thickness in mm.	Current in Amp. $\times 10^{-13}$.
Ebonite	1.05	17.8
"	2.94	70.0
"	5.07	33.5
Mica	0.6	18.8
Sealing Wax	2.85	35.2
Wax	4.7	2.3
Resin	4.75	16.4
Glass * (various kinds) .	0.12 to 0.35	4.5 to 19.9

These experiments were carried out in air at atmospheric pressure. Reiger † also made observations in a vacuum, and found that, when the insulating material (glass) was illuminated by ultra-violet light, it became a source of kathode rays, for which the ratio of the charge to the mass (e/m) was measured and found to be in agreement with Lenard's value.

W. Wilson ‡ examined another insulator, shellac. He found no discharging action with ultra-violet light. This is in accordance with the fact that shellac is proportionately very transparent for ultra-violet rays. Although shellac itself is not photo-electrically active, it allows the photo-electric current to pass through it when a thin layer is laid upon a metal plate.

THE CHEMICAL RELATIONS OF PHOTO-ELECTRIC ACTIVITY

Cantor § and Knoblauch || have upheld the view that the photo-electric current is the result of oxidation. They point out that reducing agents and bodies not fully oxidised lose their negative charges rapidly; oxidising agents and bodies fully oxidised do not lose their negative charges. In discussing this view J. J. Thomson writes: "It is, however, I think, necessary to distinguish between the *power* of combining with

* For the glass plates a potential difference of 1200 volts was employed.

† Reiger, *Ann. d. Physik*, **17**, p. 947, 1905.

‡ W. Wilson, *Ann. d. Physik*, **23**, pp. 127-128, 1907.

§ Cantor, *Wien. Sitzungsber.*, **102**, p. 1188, 1893.

|| Knoblauch, *Zeit. f. Physikalische Chemie*, **29**, p. 527, 1899.

oxygen and the *act* of combination. We should expect the photo-electric substances to be oxidisable, as they lose readily negative corpuscles, and thus get positively charged and in a fit state to combine with an electro-negative substance like oxygen; there is no evidence, however, that the presence of oxygen is necessary for the photo-electric effect, in fact the evidence the other way seems quite conclusive, for substances like rubidium and potassium enclosed in highly exhausted vessels seem to retain their photo-electric power indefinitely, and any trace of oxygen originally present would soon be absorbed by the metals."

These experiments with the alkali metals also serve as evidence against the view of Chrisler * that hydrogen is essential to the production of the photo-electric current—that is, if the metal could be entirely freed from hydrogen, it would give no photo-electric current.

Special attention must be drawn to the fact that photo-electric activity is not an atomic property as is radio-activity. In compounds of the elements the activity is found to be a constitutive and not an additive property. Thus the sulphides of antimony, lead, arsenic, manganese, silver, and tin are photo-electric, while the sulphates are not. Again, hydro-chinon gives a considerable discharge, while its isomer resorcin is almost inactive. Brillouin † found that dry ice is photo-electric, while water in the liquid state is not.

Further evidence to show that photo-electric activity is a constitutive property is afforded by the work of Pohl and Pringsheim ‡ on alloys and amalgams.

With these results as regards photo-electric action we may contrast the conclusion that secondary radiation excited by Röntgen radiation (Barkla) or radium radiation (McClelland), is additive in character.

* Chrisler, *Phys. Rev.*, **27**, pp. 267–281, 1908.

† Brillouin, *Écl. Électr.*, xiii, p. 577, 1897.

‡ Pohl and Pringsheim, *Verh. Deutsch. Phys. Gesell.*, **12**, pp. 1039–1048, 1910; **15**, pp. 431–437, 1913.

SOME RELATED PHENOMENA

There are other questions connected with photo-electric action which I have been unable to deal with at length, but which may be briefly referred to here.

Many substances when used as the two poles of a voltmeter containing an electrolyte show a difference in potential when one plate is in darkness and the other illuminated. This effect has been studied by Becquerel * and Minchin,† and quantitatively for silver plates in various electrolytes by Wilderman.‡ The behaviour of the silver haloids has also been investigated by Luggin.§

Several experimenters have sought to find a change in the electrical conductivity of a solution when the latter was exposed to light. Some of the earlier results were contradictory, but investigations with fluorescent solutions carried out independently by Goldmann|| and Hodge¶ agree in the conclusion that illumination of the solution between the electrodes does not affect the conductivity, while illumination of the colouring matter in the immediate neighbourhood of the electrodes produces an electro-motive force which brings about a change in the apparent resistance. These phenomena can be explained by assuming that negative electrons are set free from the molecular groups as in the Hallwachs effect.

Arrhenius ** found that the conductivity of the silver halides was increased when they were exposed to light. Scholl †† experimented on silver iodide immersed in aqueous salt solution. He concluded that dissociation took place on exposure to light, with the production of ions of AgI and negative

* E. Becquerel, *La lumière*, 2, p. 121, Paris, 1865.

† Minchin, *Phil. Mag.*, 31, p. 207, 1891.

‡ Wilderman, *Proc. Roy. Soc.*, 74, p. 309, 1904.

§ Luggin, *Zeit. f. phys. Chem.*, 23, p. 577, 1897.

|| Goldmann, *Ann. d. Physik*, 27, pp. 449-536, 1908.

¶ Hodge, *Physical Review*, 28, pp. 25-44, 1909.

** Arrhenius, *Wien. Ber.*, 96, p. 831, 1887.

†† Scholl, *Ann. der Physik*, 16, pp. 193-237, 417-463, 1905.

electrons. Moist silver iodide shows increased conductivity when illuminated by violet light, and this is attributed for the most part to these electrons which are set free by the light. W. Wilson* has proved that silver iodide shows marked photo-electric activity when illuminated by ultra-violet light, but none when illuminated by violet light. The electrons set free by the violet light have not sufficient velocity to escape from the substance, but their presence is revealed by the increase in the electrical conductivity. Ultra-violet light also causes an increase in the conductivity, but this is small in comparison with that brought about by violet rays. The ultra-violet light is effective in separating electrons with large velocities, but these are less easily controlled by the applied electric field than the slower electrons, and so the conductivity is not greatly changed.

Ordinary metals show no increase in electrical conductivity when illuminated, though electrons are liberated, simply in consequence of the fact that the number of free electrons is already so large that the addition of the photo-electrons makes no appreciable difference in the total. In the case of the granular silver examined by W. Wilson,† light does produce an increase of conductivity, no doubt in consequence of the passage of electrons from grain to grain.

The sensitiveness of selenium to light, as shown by the changes in the electrical conductivity, has been the subject of a very great number of investigations. The explanation put forward independently by Berndt‡ and by Marc,§ is based on the assumption that there are a number of allotropic modifications of selenium, and that light brings about a transformation from one variety to another. On the other hand, Ries|| supports the view that the change of conductivity is due to the liberation of slowly moving electrons, which remain within the substance and thus increase its conducting power. This theory would bring the behaviour of selenium into line

* W. Wilson, *Ann. d. Physik*, **23**, pp. 107-130, 1907.

† *Ibid.*

‡ Berndt, *Phys. Zeit.*, **5**, pp. 121-124, 1904.

§ Marc, *Zeit. Anorg. Chem.*, **37**, pp. 459-475, 1903; **48**, pp. 393-426, 1906.

|| Ries, *Phys. Zeit.*, **12**, pp. 480-490, 1911.

with other photo-electric actions. It is supported by the facts that no evolution of heat can be detected in the supposed transformations, and that selenium is sensitive to light at the temperature of liquid air. An adequate discussion of the complicated and difficult questions here involved is beyond the scope of the present work.

CHAPTER VII

PHOTO-ELECTRIC SUBSTANCES—GASES AND VAPOURS

PHOTO-ELECTRIC ACTIVITY OF GASES

THE question whether gases show any photo-electric activity is a very important one. Since we have to deal with isolated molecules instead of with matter in bulk, we might expect investigations on this subject to give valuable information as to the mode of liberation of electrons from the molecule. The effect is, however, extremely small in the cases so far investigated, and the experimental difficulties are great.

If some of the molecules of a gas lose negative electrons when irradiated by ultra-violet light, we should expect the gas to show increased conductivity. At ordinary pressures the electron will probably soon become attached to another molecule, forming a negative ion, while the molecule from which it escaped will act as a positive ion. Thus the gas would be ionised.

Lenard* experimented on gases, using ultra-violet light of short wave-length derived from a spark between aluminium terminals. The light passed through a layer of air 2 mm. thick and through a quartz window. In order to prevent any photo-electric action from surfaces on which the light fell, they were covered with soap and water. A charged conductor outside the quartz window lost a positive charge more rapidly than a negative. This was explained by assuming a greater velocity for the negative ion than for the positive. According to Lenard, air, oxygen, carbonic acid gas, hydrogen, and coal gas are all ionised in this way.

These results have been much criticised. J. J. Thomson†

* Lenard, *Ann. der Physik*, **1**, p. 486 ; **3**, p. 298, 1900.

† J. J. Thomson, *Conduction of Electricity through Gases*, p. 254.

holds that the small velocity of the positive ions observed by Lenard points to the presence of dust particles or small drops of impure water. Bloch* has investigated the question experimentally, and attributes Lenard's results to dust particles in the gas. Stark† also criticises the conclusions on the ground that the light would have very small intensity for wave-lengths less than $180\text{ }\mu\mu$. But light of greater wave-length is not absorbed by hydrogen, which according to Lenard shows as much ionisation as carbonic acid gas.

Schumann has proved that light from near the kathode of a vacuum tube contains a large proportion of waves of extremely short wave-length (less than $180\text{ }\mu\mu$). The effect of this radiation was first investigated by F. Palmer,‡ who found that considerable ionisation of air is produced by waves shorter than $185\text{ }\mu\mu$, and that the amount increases as the wave-length decreases. Lyman§ has shown that the radiation, issuing through a fluorite window from a vacuum tube containing hydrogen at 2 mm. pressure, ionises the air just outside the window. If this air is blown against a charged plate connected with an electroscope, the latter rapidly loses its charge. A piece of microscope cover glass 0.2 mm. thick placed on the fluorite window is sufficient to annul the effect. The active rays are largely absorbed within 1 mm. of the window.

J. J. Thomson,|| in a paper on the ionisation of gases by ultra-violet light, describes experiments by G. W. C. Kaye in which the source of light was a vacuum tube provided with a Wehnelt kathode which was raised to a white heat. With this arrangement a comparatively small potential difference (300 volts) produced a large current (about 0.1 ampere) through the discharge tube. The light passed through a quartz window 0.4 mm. thick into a small box, through which a current of dry dust-free gas was made to flow. The gas then flowed between two concentric cylin-

* Bloch, *C. R.*, **146**, p. 892, 1908.

† Stark, *Phys. Zeit.*, **10**, pp. 614-623, 1909.

‡ Palmer, *Nature*, **77**, p. 582, 1908.

§ Lyman, *Astro-physical Journal*, **28**, p. 52, 1908.

|| J. J. Thomson, *Camb. Phil. Soc. Proc.*, **14**, pp. 417-424, 1908.

drical tubes, the outer charged to 100 volts, the inner connected to an electroscope.

With air the natural leak was increased 8 times as the maximum, when the gas was exposed to ultra-violet light.

With carbonic acid the natural leak was increased as much as 16 times by the ultra-violet light.

With ammonia the natural leak was increased as much as 150 times by the ultra-violet light.

The ultra-violet light is absorbed by a few millimetres of air at atmospheric pressure, and is absorbed still more strongly by coal gas. The greater portion of the effective ultra-violet light came from quite close to the *anode*.

Further experiments were carried out at Cambridge by A. L. Hughes,* who was unable to obtain definite indications of ionisation of air due to ultra-violet light which had passed through thin quartz plates. But one particular plate of fluorite was obtained which transmitted ultra-violet light capable of producing positive as well as negative ions in air. If negative ions alone are produced by the light they may be due to surface ionisation, but the presence of positive carriers indicates an actual ionisation of the air by the ultra-violet light. Special experiments with a Wilson expansion apparatus were carried out to show that dust particles had been effectually removed. The mobilities of the positive ions produced by ultra-violet light and by X-rays were found to be identical. According to Hughes, the ionisation of air by ultra-violet light sets in at about wave-length $135 \mu\mu$. If we assume that this critical wave-length is associated with the oxygen of the air, and that Einstein's formula with Planck's constant can be applied to this case, the ionising potential may be calculated, and is found to be 9.2 volts (Hughes). This agrees well with the value, 9.0 volts, found for oxygen by Franck and Hertz.†

The conclusion of Hughes that the ionisation of air by light cannot be produced by light whose wave-length is greater than about $135 \mu\mu$ is not accepted by Lyman.‡ Palmer has

* Hughes, *Proc. Camb. Phil. Soc.*, **15**, pp. 483-491, 1910; *Phil. Mag.*, **25**, p. 685, 1913.

† Franck and Hertz, *Deutsch. Phys. Gesell. Verh.*, **15**, p. 34, 1913.

‡ Lyman, *Phys. Zeitschr.*, **13**, pp. 583-584, 1912; *Nature*, **91**, p. 371, 1913.

found a small but perfectly definite volume ionisation using the light from a mercury arc, and Lyman has been unable to discover any lines in the spectrum of the arc below $140\ \mu\mu$. According to Bloch* ionisation is produced by the light from an arc in quartz—that is, by light whose wave-length is longer than $170\ \mu\mu$.

The volume ionisation produced in a gas by light of extremely short wave-length has been carefully studied in a later investigation by F. Palmer.† The source of light was a discharge tube containing hydrogen. There are strong hydrogen lines from $165\ \mu\mu$ to $125\ \mu\mu$. The light passed from the discharge tube through a window of clear white fluorite into a “screen cell” containing oxygen. By varying the pressure of the oxygen in this cell more or less of the effective rays could be cut off. From this cell the light passed through a second fluorite window into the ionisation chamber. A current of gas was passed through the ionisation chamber, and thence, with the ions there produced, into the testing cylinders. The Hallwachs effect was eliminated by coating the surfaces exposed to light with soap solution. The experiments showed marked ionisation in air and oxygen, practically none in hydrogen, and an unexpectedly large effect in nitrogen. This may be due to strong absorption in nitrogen for wave-lengths between $150\ \mu\mu$ and $130\ \mu\mu$. The extremely small ionisation observed with hydrogen proves that the effects with the other gases cannot be due to photo-electric action at the surfaces of the ionisation chamber or to dust. The insertion of a long plug of cotton-wool in the stream of gas was without influence, again proving that dust had been effectively removed. Curves were obtained showing the ionisation produced for various pressures of the oxygen in the screen cell. It was found that the power of ionisation increases greatly with decrease in wave-length, so that the currents obtained were large compared with the values of other observers.

If a gas in the luminous state emits rays which are photo-

* Bloch, *C. R.*, **155**, p. 1076, 1912.

† F. Palmer, *Phys. Rev.*, **32**, pp. 1–22, 1911.

electrically active, it might be expected, if the emission of electrons is a resonance effect, that the same gas when exposed to these particular rays would show greater photo-electric activity than when it is exposed to rays from other sources of light. In order to test this point Cannegieter* constructed an apparatus consisting of a discharge tube, an absorption space, and an ionisation chamber. Each part was airtight, and could be filled with any desired gas. No selective effect of the kind sought for was observed in these experiments.

An elaborate investigation carried out by Lenard† in collaboration with C. Ramsauer at the Radiologisches Institut of Heidelberg explains many of the earlier difficulties in connection with the action of light on gases, and shows that, in consequence of the presence of small traces of impurities, the effects are often very complicated.

Three different actions of ultra-violet light on dust-free gases may be distinguished :

1. The formation of electrical carriers of molecular size, caused by selective absorption of the light.
2. Chemical action—*e.g.* formation of ozone in oxygen.
3. The formation of condensation nuclei, that is the formation of solid or liquid products by the direct action of the light on the gases.

It is extremely difficult to remove the last traces of easily condensed gases and vapours, such as CO_2 , NH_3 , organic vapours, and H_2O , present in small quantities in the air. Even if the air is carefully purified it is liable to contamination again, for the walls of the vessel spontaneously give off traces of vapour which they have previously absorbed from the air, unless such surfaces are heated to dull redness. These impurities lead to the formation of nuclei, originally uncharged,

* Cannegieter, *Konink. Akad. Wetensch. Amsterdam, Proc.*, **13**, pp. 1114-1119, 1911.

† P. Lenard and C. Ramsauer, " Ueber die Wirkungen sehr kurzwelligen ultra violetten Lichtes auf Gase und über eine sehr reiche Quelle dieses Lichtes," *Heidelberger Akademie*, 1910-1911. C. Ramsauer, *Phil. Mag.*, **23**, pp. 849-852, 1912.

when the air is exposed to ultra-violet light. These molecular aggregates are not formed in very pure air.

The experimental results already recorded show that ionisation will be produced in the atmosphere of the earth by the solar rays. In the outer regions of the atmosphere there will be direct ionisation of the gases through the action of the extreme ultra-violet rays, and somewhat lower down there will be indirect ionisation due to the presence of dust particles which show photo-electric activity for longer wavelengths. There will also be the formation of condensation nuclei, such as drops of hydrogen peroxide formed from water vapour under the influence of ultra-violet light. These complicated effects produced in the atmosphere by sunlight (and also to a certain extent by kathode radiation from the sun) raise important and interesting questions in connection with meteorological phenomena * and the propagation of electromagnetic waves round the earth.† Marconi in 1902 observed marked differences in the transmission of artificial electromagnetic waves over long distances by day and by night, the signals being more easily read by night. Striking effects have also been found about the time of sunrise and sunset. Eccles has observed corresponding diurnal variations in the number and intensity of the natural wave-trains, or "strays" received at particular stations. These remarkable results no doubt depend in some way not yet clearly understood on changes in the state of ionisation of the atmosphere. At sea-level the air is only slightly ionised, while at the height of a few miles it is found by observations from balloons that the ionisation is sometimes 20 times that at the surface. At greater heights the ionisation is doubtless still larger. Eccles supposes that during the day the electric waves travel in a comparatively thin shell between the middle atmosphere and the surface of the earth, while at night they travel in the much wider shell below the high conducting layer postulated by Heaviside. Electric radiation starting from a point on the earth's surface is supposed to suffer refraction downwards

* Ramsauer, *Nature*, **88**, p. 212, 1911.

† Eccles, *Proc. Roy. Soc., A*, **87**, pp. 79-99, 1912.

when it reaches the ionised stratum of the atmosphere. By means of some such assumptions it may be possible to account for the phenomena.

For a discussion of the bearing of photo-electric phenomena on atmospheric electricity the reader may be referred to a small volume recently published by Dr. Karl Kähler.*

PHOTO-ELECTRIC ACTIVITY OF VAPOURS

The study of photo-electric phenomena would be greatly facilitated were it possible to study conveniently ionisation by light in a gas or vapour. The ionisation of gases can only be produced by ultra-violet light of very short wave-length.

Only a few vapours are known in which ionisation can be produced by the action of light. Sodium vapour shows increased conductivity when illuminated by ordinary light. Stark† has shown that there is a true photo-electric effect in the case of anthracene, diphenylmethane, α -naphthylamine, and diphenylamine. The light producing ionisation has wave-length between 180 and 380 $\mu\mu$. Steubing‡ has shown that fluorescing mercury vapour is ionised. In these experiments the apparatus has to be kept at a high temperature, so increasing the difficulties of the experiment. Iodine vapour,§ though it absorbs much light, shows no increase in conductivity when illuminated. Whiddington|| examined fluorescing iodine vapour, but no trace of ionisation could be detected even when the applied electric field was almost enough to produce a discharge. In this experiment the light from an arc lamp appears to have been filtered through the glass wall of the tube, so that no short wave-lengths were made use of.

Reference must also be made to some interesting results obtained by G. Owen and H. Pealing,¶ who found that when moist air (or oxygen) containing iodine vapour is illuminated,

* Kähler, *Luftelektrizität*, pp. 140-144. Sammlung Götschen, Berlin und Leipzig, 1913.

† Stark, *Phys. Zeit.*, **10**, pp. 614-623, 1909.

‡ Steubing, *Phys. Zeit.*, **10**, pp. 787-793, 1909.

§ Henry, *Proc. Camb. Phil. Soc.*, **9**, p. 319, 1897.

|| Whiddington, *Proc. Camb. Phil. Soc.*, **15**, p. 189, 1909.

¶ G. Owen and H. Pealing, *Phil. Mag.*, **21**, pp. 465-479, 1911.

uncharged nuclei are produced which are very unstable, disappearing in a few seconds in the dark. The presence of the nuclei was rendered evident by suddenly expanding the air in a Wilson expansion apparatus. This effect seems to depend on the presence of small traces of impurity on the glass walls of the vessel or on the glass-wool used as a filter for the air.*

The production of uncharged condensation nuclei in the presence of vapours must be regarded as a photo-chemical effect which is only indirectly related to photo-electric action. Such cases have been studied by Tyndall,† Aitken,‡ and C. T. R. Wilson.§

With a view to detecting ionisation due to photo-electric action, Hughes|| examined the vapours carbon bisulphide, carbon dioxide, tin tetrachloride, and zinc ethyl. The source of light was a mercury arc in quartz, and the ionisation chamber was provided with a quartz window, the shortest wave-length¶ employed being $184.9 \mu\mu$. In no case was any trace of ionisation detected. For the same amount of light energy, the leak from a zinc or carbon surface would be about a million times that of the smallest effect which could be measured in these experiments.

* Cf. C. Ramsauer, *Phil. Mag.*, **23**, p. 852, 1912.

† Tyndall, *Phil. Trans.*, **160**, p. 337, 1870.

‡ Aitken, *Proc. Roy. Soc. Edin.*, **39**, (1), p. 15, 1897.

§ Wilson, *Phil. Trans.*, **192**, p. 403, 1899.

|| Hughes, *Proc. Camb. Phil. Soc.*, **16**, pp. 376-383, 1911.

¶ *Proc. Camb. Phil. Soc.*, **16**, pp. 428-429, 1911.

CHAPTER VIII

THE INFLUENCE OF TEMPERATURE ON THE PHOTO-ELECTRIC DISCHARGE

THE experimental investigation of the influence of temperature on photo-electric activity is of great importance, as the results have a direct bearing on any attempt to elucidate the mechanism of the discharge.

Adopting the view that the photo-electric current is due to the emission of negative electrons from the illuminated surface, we see that there are several ways in which the current might be affected by temperature. A change in temperature may cause (1) a change in the number of electrons emitted, (2) a change in the initial velocity of these electrons, (3) when the discharge is carried through a gas, changes in the number, character, and velocity of the ions formed in the gas by adhesion or collision.

In addition to the direct action of temperature on the photo-electric current there may be secondary actions—*e.g.* actions due to chemical or physical changes in the state of the metal surface, or of the gas in contact with it.

When experiments are carried out in gases at ordinary pressures it is very difficult to disentangle these effects, and it is not surprising that contradictory results have been obtained. It is only from experiments carried out in a high vacuum that we can hope to obtain clear indications as to the relations between photo-electric activity and temperature.

The early experiments on the influence of temperature were carried out at ordinary pressures. Hoor* records an experiment in which a zinc plate was warmed to 55° C., and its activity measured as it cooled to the temperature of the room (18° C.). He observed a considerable increase in the activity

* Hoor, *Wien Berichte*, 97, p. 719, 1888.

as the temperature diminished. Stoletow* made experiments on the influence of temperature with platinum plates. The apparatus was placed in an air-bath and gradually heated to 200° C. The photo-electric effect was found to increase, but the changes were somewhat complicated, and secondary maxima and minima were observed. Righi† found that the positive potential, acquired under the influence of light by an uncharged plate in air, increased with the temperature.

Elster and Geitel‡ found no alteration with temperature in the discharge current from zinc. On the other hand, they observed that the activity of a photo-electric cell containing potassium increased with rise of temperature up to about 60° C. In this case the metal was contained in a vessel containing gas at the "critical" pressure of 0.3 mm. of mercury.

J. J. Thomson§ states that when the temperature is raised to about 200° C. there is a very great increase in the current from the alkali metals.

Experiments in air at atmospheric pressure were carried out by Zeleny|| on platinum and iron wires heated by means of an electric current. With a platinum wire the photo-electric current at first diminishes as the temperature rises; it reaches a minimum between 100° C. and 200° C., and subsequently increases up to about 700° C., when its value is about twice that at the temperature of the room (Fig. 24). A limit to the temperatures that can be employed is imposed by the fact that the wire begins to discharge electricity due to heat alone, and when this effect is large it is difficult to distinguish it from the true photo-electric effect.

The rate of discharge due to light at any temperature depends on the previous history of the wire. This is illustrated by the curves in Fig. 25. When a certain temperature is reached by cooling the wire down from a higher temperature, the current is much greater than if the wire had been heated up to the same temperature. The most marked difference in

* Stoletow, *C. R.*, **108**, pp. 1241-1243, 1889.

† Righi, *Journal de Physique*, **10**, p. 538, 1891.

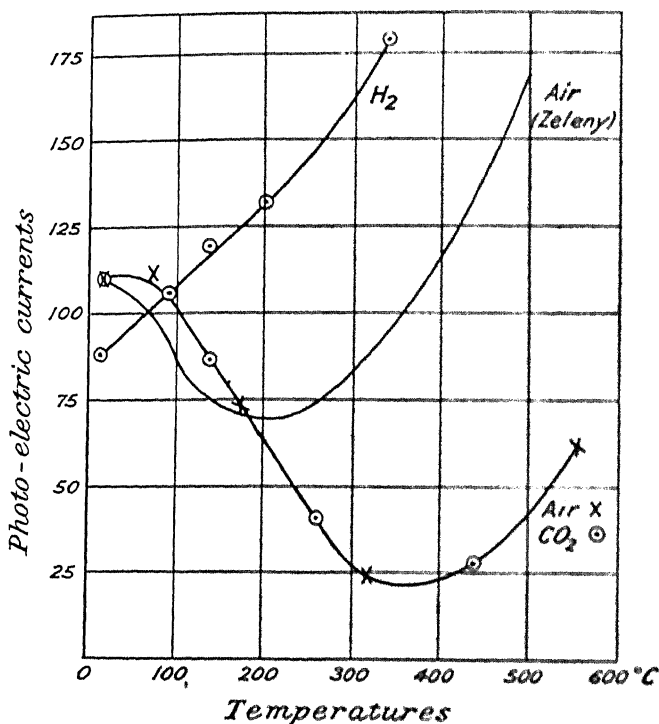
‡ Elster and Geitel, *Wied. Ann.*, **48**, p. 634, 1893.

§ J. J. Thomson, *Conduction of Electricity through Gases*, p. 239.

|| Zeleny, *Physical Review*, **12**, pp. 321-339, 1901.

the curves appears at a temperature of about 100°C ., "indicating that at this temperature some more or less sudden change in the conditions takes place." An obvious suggestion to make is that the change is connected with the condensation of water vapour.

From an iron wire the rate of discharge diminishes somewhat as the temperature is raised, but after passing a minimum



Royal Society of Edinburgh.

FIG. 24

it increases fairly rapidly and becomes many times as great as at the temperature of the room, the current at 700°C . being about 40 times that at 15°C .

Iron did not show the same tendency as platinum for readings taken with decreasing temperatures to exceed those taken with increasing temperatures.

Varley and Unwin* carried out many series of observations

* Varley and Unwin, *Proc. Roy. Soc. Edin.*, **27**, pp. 117-134, 1907.

on the photo-electric current from platinum at different temperatures, using various gases and making the tests (1) at atmospheric pressure, (2) at a pressure of about 50 mm. of mercury, (3) at very low pressures. The temperature of the metal, which was a piece of platinum foil, was varied between 5° and 500° C. by passing through it the current from two large secondary cells. Measurements of temperature were

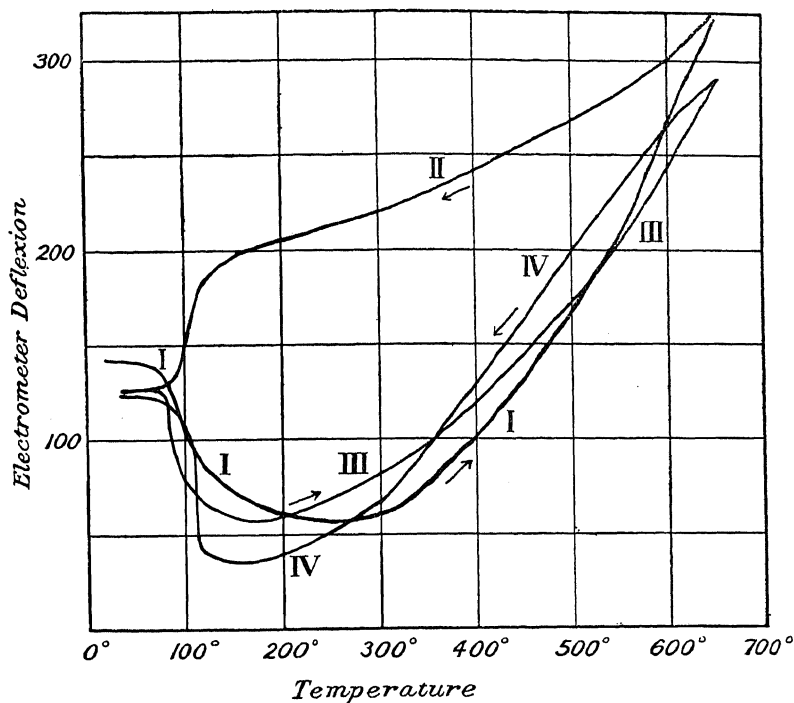


FIG. 25

made by means of a platinum-rhodoplatinum junction. As Varley had previously found that satisfactory results could not be obtained at low pressures by using wire or gauze electrodes, owing to the electrons passing through the meshes of the gauze, in these experiments the second electrode was a copper disk. The source of light was a discharge between iron terminals in an atmosphere of hydrogen.

The final value of the photo-electric current was not attained for some minutes after increasing the heating current,

though the platinum took up its final temperature within a few seconds.

The curve obtained from experiments in air at atmospheric pressure resembles in form that given by Zeleny, but the minimum is at a temperature about 200° higher (Fig. 24). This may be explained by the fact that Zeleny used a voltage of 72 volts for a distance of 1.6 cm., which would be insufficient to give a saturation current, and that in his experiments the readings were taken at short intervals, the whole series only occupying about twenty minutes.

The results in carbon dioxide at atmospheric pressure were very similar to those in air at the same pressure. If the actual values of the currents observed in carbon dioxide are multiplied by 1.22 and then plotted against the temperature, the points fall on the curve for air (Fig. 24).

In hydrogen the current increases steadily with temperature from the ordinary temperature of the room, the experiments being made in gas at atmospheric pressure.

When the pressure was reduced to somewhat less than 50 mm. of mercury the results were similar to those at the higher pressure, but neither in carbon dioxide nor in air was a point reached at which the current began to increase with the temperature.

In the experiments carried out at very low pressures the nature of the residual gas was found to have comparatively little influence on the result.

When a small heating current was passed through the platinum the sensibility at first increased, but when a temperature of 60° C. was reached no further increase occurred, the sensibility remaining constant from 60° C. to at least 350° C.

It is pointed out that the passage of the heating current through the platinum may produce a change in sensibility apart from the rise of temperature produced.

Interesting results were obtained by Lienhop* from experiments carried out at low temperatures on carbon and iron. He established the fact that both the photo-electric current

* Lienhop, *Annalen der Physik*, 21, pp. 281-304, 1906.

from, and the positive potential acquired by, these substances are independent of the temperature, from the temperature of the room down to the temperature of liquid air. This was done by obtaining the velocity distribution curves, both at ordinary temperatures and at very low temperatures, secured by the use of liquid carbonic acid and liquid air. The resulting curves were of practically the same form at these widely different temperatures.

Dember* found no influence of temperature in a very high vacuum in the case of the alkali metals exposed to light. This result holds for sodium between 26° and 110° (sodium becomes fluid at 96°), for potassium between 34° and 70° , and for sodium-potassium alloy between 20° and 80° . The experiments of Elster and Geitel showing a change with temperature were not carried out in the highest vacuum but at the "critical" pressure, .3 mm.

Millikan and Winchester† carried out an investigation on the influence of temperature on photo-electric effects in a high vacuum. The vacuum was produced by a specially designed mercury pump made entirely of glass, and could be maintained for months, the pressure registered by a MacLeod gauge being .00001 mm. The first experiments were made with an electrode of aluminium, and went to show that temperature had no effect whatever upon the rate of discharge of electrons from aluminium, between 50° C. and 343° C.

Experiments were afterwards made so as to obtain results for a series of metals under identical conditions. The metals used were copper, nickel, iron, zinc, silver, magnesium, lead, antimony, gold, aluminium, and brass. The natural leak of the system became so great at temperatures above 150° C. that it could not be allowed for with certainty. Between 25° C. and 125° C. rise of temperature had no effect on the discharge of negative electricity from the metals named above, the observational error being seldom more than 2 per cent.

These investigators also examined the effect of tempera-

* Dember, *Annalen der Physik*, **23**, p. 957, 1907.

† Millikan and Winchester, *Phil. Mag.*, **6**, **14**, pp. 188-210, 1907.

ture on the velocity of projection of electrons from different metals. The maximum velocity was determined by measuring the positive potential assumed under the influence of light.

Between 25° C. and 100° C. the positive potential was found to be completely independent of temperature, the observational error here being less than 1 per cent. The average time taken to acquire a permanent positive deflection of the electrometer needle was about 90 seconds.

Ladenburg * carried out an investigation on the photo-electric effect at high temperatures. Referring to the contradictory results of previous experimenters, he points out that a rise of temperature may alter the surface of the plate, and in particular may free it from occluded gases. His experiments are carried out in a vacuum so good that the free paths of the electrons is greater than the distance between the electrodes. A mercury vapour lamp of quartz was used to illuminate the plate E through the quartz window Q (Fig. 26).

The leak was measured by a sensitive Dolezalek electrometer, using Bronson's method. In this method a high resistance is employed, consisting of an air condenser (W, Fig. 26) in which the air is ionised by a radio-active salt (R). The resistance in this case amounted to 4.55×10^9 ohms.

Electrodes of platinum, gold, and iridium were used, and they could be heated by a current from accumulators. The plates were about .01 mm. thick and .8 × .3 cm. in area. The temperature was determined by measuring the resistance. In order to free the plates from occluded gases they were heated for several hours before an experiment, an automatic pump being at work the whole time. If air or hydrogen is allowed to remain occluded in a (platinum) plate, the photo-electric activity may be 50 per cent. greater than with a gas-free plate.

It was impossible to test the photo-electric activity for temperatures above 800° C., since at higher temperatures discharge takes place without illuminating the plate.

* Ladenburg, *Deutsch. Phys. Gesell. Verh.*, 9, pp. 165-174, 1907.

As the temperature is raised from 20°C . the activity increases to a maximum at about 100°C . and then diminishes. By repeating the heating and cooling several times in succession, this maximum becomes less marked, and finally disappears almost entirely. On allowing the plate to stand for a time and repeating the experiment the maximum again makes

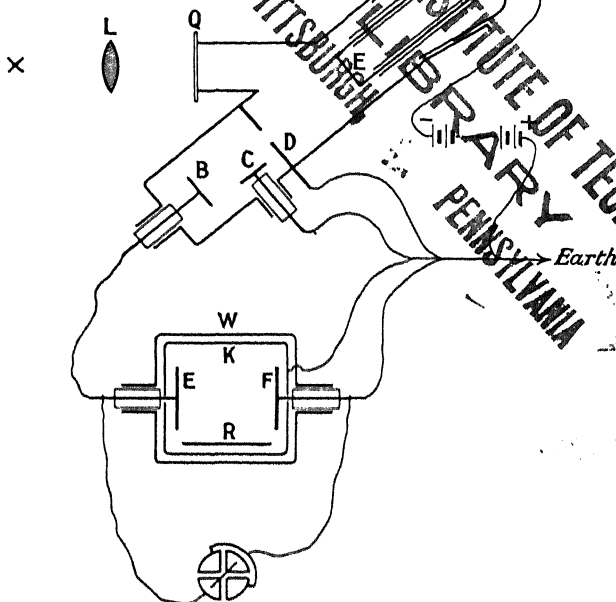


FIG. 26

its appearance. Since it occurs at about 100°C ., Ladenburg attributes it to water vapour. Iridium and gold gave results similar to platinum. It is concluded that the number of electrons emitted from these metals is independent of the temperature of the illuminated plate up to about 800°C . The velocity of the electrons emitted was measured at various temperatures by determining the magnetic deflection, as in the experiments of Lenard. No alteration in velocity with temperature could be observed.

Jakob Kunz* found that the positive potential acquired by sodium-potassium alloy does not increase with increasing temperature; there was rather a slight decrease of the deflection, attributed to increasing conductivity of the glass wall of the cell.

Reviewing the experimental work available as to the influence of temperature on photo-electric effects, the balance of evidence is in favour of the view that, when secondary actions are eliminated, the number of electrons and the velocity of emission are independent of the temperature.

Incidentally we may notice that the alteration of resistance of selenium when exposed to an arc lamp is independent of temperature, from the temperature of the room down to -185°C. † Further, the effects of phosphorescence, which according to Lenard's theory is intimately connected with photo-electric emission, can be observed at the lowest obtainable temperatures, certainly at the temperature of solid hydrogen.

The results are to be explained, according to Lienhop, by assuming that the electrons emitted under the influence of light are quite different from those that bring about the emission of light when the temperature is raised. The internal energy of the electrons of the photo-electric discharge is not affected by temperature.

Ladenburg prefers a different explanation. Active light has a very high frequency. The electrons in the illuminated plate are in a certain state of vibration at a definite temperature. A certain proportion of them are caused to resonate by the incident light and are discharged. If the temperature is raised to 800°C. , more electrons will vibrate with a higher frequency than at lower temperatures; but the increase in the number of resonating electrons is too small to be observed.

The negative electrons liberated from a metal exposed to radiation may be attributed to two possible sources. They may come from the "free" or "metallic" electrons, to which the conductivity of the metal is due, or they may be derived

* Jakob Kunz, *Phys. Rev.*, **29**, pp. 174-6, 1909.

† Pochettino, *Rend. R. Acc. dei Lincei*, **11**, p. 286, 1902.

from atomic systems which become unstable under the influence of the radiation.

According to the first view, the free electrons by absorbing energy from the incident light must acquire a velocity sufficiently great to enable them to escape from the metal surface. If the temperature is raised the kinetic energy of the free electrons is increased, as these are supposed to be subject to the ordinary gas laws, and a smaller increase in energy would be required to permit them to escape. Thus we should expect the number of electrons emitted in unit time to increase as the temperature rises. But if the energy of a "free" electron in the metal is small compared with the work an electron would have to do to escape, this increase would be a small one and might only become appreciable at high temperatures, when thermionic emission would be on the point of taking place.

If, however, the electrons are, as it were, expelled from the atoms by a species of instability induced by the incident light, we should not expect temperature to have any influence on the number or velocity of the electrons liberated, since we have no reason to believe that the internal energy of the atom is dependent on temperature.

CHAPTER IX

THE INFLUENCE OF THE CHARACTER OF THE LIGHT ON THE PHOTO-ELECTRIC DISCHARGE

IN order to form a theory as to the way in which light-waves bring about the liberation of electrons from photo-electric substances, it is essential to study the relation between the photo-electric discharge and the character of the light employed. We must examine the influence of the light both on the number of the electrons expelled and on the velocity with which they leave the substance. For each of these factors we must investigate what change, if any, is brought about by varying (1) the intensity, (2) the plane of polarisation, (3) the frequency of the exciting light.

Before beginning the study of these relations it will be convenient to pass in review the sources of light * that have been employed in photo-electric experiments.

SOURCES OF LIGHT

Except when experiments are made with the more electro-positive metals, we require a source of light which shall be rich in ultra-violet rays. The light of burning magnesium may be used for qualitative experiments, but for quantitative work a more constant source is required. We have seen that sunlight has sometimes been employed, but most of the ultra-violet rays from the sun are absorbed by the atmosphere. The author has employed the light of a powerful Nernst lamp supplied with current from a battery of accumulators, but the photo-electric effects obtained with zinc or aluminium are not large, currents of the order of 10^{-12} amperes being usual with

* Sources of light suitable for photo-chemical experiments have been discussed by Dr. Johannes Plotnikow in his book *Photo-chemische Versuchstechnik*, Leipzig, 1912.

plates 5 cm. in diameter. W. A. Scoble has photographed the spectrum of the lamp; in no case was any effect produced beyond wave-length $210\ \mu\mu$, and the results were comparatively faint from at least $250\ \mu\mu$. By far the greatest photographic effect was obtained in the visible violet and blue.

The three sources most frequently employed are the arc, the spark, and the mercury vapour lamp. The arc was used by Hertz and Hallwachs. Righi used an arc between carbon and a rod of zinc, Bichat and Blondlot used a positive carbon with aluminium core.

The photo-electric radiation from the arc has been made the subject of a research by R. Lindemann.* The photo-electric current from a sensitive (CuO) plate was measured and plotted against the potential difference, current strength, and length of arc respectively. Arcs between impregnated carbons produce a smaller photo-electric current than arcs between homogeneous carbons. The greatest effect is due to the light from the violet tufts at the extremities of the electrodes, which consist of unburnt carbon vapour, and not to that from the surrounding aureole.

Varley † recommends as a constant source of light an arc between iron terminals, preferably in an atmosphere of hydrogen. In his experiments the terminals were connected to the secondary terminals of an induction coil with three large Leyden jars arranged in parallel. An alternating current of 4 amperes passed through the primary coil. The ultra-violet light obtained from this source remained practically unaltered in intensity for hours and even days. But the arc could not be run continuously; it was usually employed for ten-second periods every few minutes.

The spark was used as a source of light in the original experiments of Hertz, and many later experimenters have employed a spark between terminals of aluminium, zinc, or cadmium. Lenard used a 6 mm. spark between zinc terminals; in other experiments he employed a spark between aluminium terminals, emitting a very easily absorbed radia-

* R. Lindemann, *Ann. d. Physik*, **19**, 4, pp. 807-840, 1906.

† Varley, *Phil. Trans.*, A, **202**, pp. 439-458, 1904.

tion which is inappreciable after passing through a few centimetres of air. Kreusler and Branly used a spark between aluminium terminals.

The spectra from sparks between metallic terminals have been photographed by Lyman* in the extreme ultra-violet or Schumann region. In the case of the aluminium spark the spectrum contained some strong lines between $185\ \mu\mu$ and $160\ \mu\mu$, but between $160\ \mu\mu$ and $125\ \mu\mu$ there was only one group of any strength, at about $130\ \mu\mu$.

In examining the effect of various wave-lengths of the exciting light, Hughes† found that reliable results could not be obtained when the spark was used as a source. Millikan‡ has given an account of some remarkable effects produced by using very powerful sparks, which caused the emission of electrons with velocities unusually large. He has since shown that these anomalous results are due to imperfect screening from electro-magnetic waves, and that when a powerful spark is used as a source of light very great precautions are necessary to avoid this source of error.

The introduction of the mercury vapour lamp has provided a very convenient source of ultra-violet radiation, which possesses the advantage that the light intensity can be maintained approximately constant over long periods of time. It is of course necessary for constancy that the pressure of the electric supply should remain unchanged. When current is supplied to such a lamp from a battery of accumulators, I find that from fifteen to twenty minutes must elapse before a steady state is attained, and even after that time there appear to be small variations, roughly periodic in character with a period of about ten minutes, in the intensity of the light emitted.

Mercury vapour lamps can be obtained constructed of ordinary glass, of Uviol glass, which transmits considerable ultra-violet radiation, and also of fused quartz.

* Lyman, *Phys. Zeitschr.*, **13**, pp. 583-584, 1912; *Astrophys. Journ.*, **35**, pp. 341-353, 1912; *Nature*, **91**, p. 371, 1913.

† Hughes, *Phil. Trans. Roy. Soc.*, **212**, p. 205, 1912.

‡ Millikan, *Phys. Rev.*, **84**, p. 68, 1912; **85**, p. 74, 1912; (2) **1**, pp. 73-75, 1913.

Photometric measurements made with the quartz lamps of the firm of W. C. Heraeus have been given by R. Küch and T. Retschinsky* both for visible and ultra-violet radiation.† The spectrum has been photographed and measured as far as wave-length $334 \mu\mu$ by J. Stark,‡ using a three-prism spectroscope constructed of Jena ultra-violet glass.

T. M. Lowry§ has photographed the spectrum of a lamp in my possession, using lenses and prism of quartz. With a short exposure a well-marked line spectrum was obtained, extending to about $240 \mu\mu$.

Hallwachs|| has published reproductions showing the ultra-violet spectrum, photographed with exposures from 1 to 256 seconds. In the last case a faint line appears at $221 \mu\mu$.

The emission in considerable quantity of waves of still shorter wave-length is shown by the production of a large amount of ozone, indicating the presence of light of wave-length less than $200 \mu\mu$ (see p. 203, Chapter XIV). This renders it advisable in some cases to place the lamp outside the room in which work is being carried on. Care must be taken to avoid more than a momentary exposure of the naked eye, or even the skin of the body, to the direct light from the lamp.

Hughes¶ has shown that the light from the mercury arc in fused quartz extends to wave-length $184.9 \mu\mu$, where he finds a line that can produce a definite impression on a photographic plate. The most refrangible line observed by Lyman** is at $177.5 \mu\mu$.

Only a few experimenters have attempted to use the extremely short waves investigated by Schumann and Lyman. These waves are absorbed by a few millimetres of air at ordi-

* Küch and Retschinsky, *Ann. der Physik*, **20**, pp. 563-583, 1906; **22**, pp. 595-602, 852-866, 1907.

† See also V. Henri, *C. R.*, **153**, pp. 265-267, 426-429, 1911.

‡ J. Stark, *Ann. der Physik*, **4**, **16**, pp. 490-515, 1905.

§ See the Royal Institution lecture summarised in *Nature*, **91**, pp. 543-544, 1913, where a similar photograph is reproduced.

|| Hallwachs, *Ann. d. Physik*, **30**, pp. 598-601, 1909.

¶ Hughes, *Proc. Camb. Phil. Soc.*, **16**, p. 428, 1912.

** Lyman, *Nature*, **91**, p. 371, 1913.

nary pressures. They can be produced by passing an electric discharge through a vacuum tube containing hydrogen (as far as wave-length $100\ \mu\mu$) or mercury vapour (a strong spectrum between 165 and $103\ \mu\mu^*$). Unless the plate under test is actually in the same vacuum as that through which the discharge passes it is necessary to use a window to separate the discharge tube from the chamber containing the test-plate. Fluorite, the most transparent substance known, only transmits as far as $123\ \mu\mu$, and it is very difficult to obtain good specimens. Quartz comes next to fluorite in order of transparency. Plates of quartz $1\ \text{mm.}$ thick will transmit as far as $150\ \mu\mu$, but the absorption rapidly increases with the thickness.

Hughes \dagger has made experiments in which the mercury arc and the metal plate under test were placed in the same vacuum. By assuming Ladenburg's law (p. 130), which is at any rate approximately true over the range investigated, he finds that the ultra-violet spectrum of mercury, investigated electrically, extends to about $123\ \mu\mu$. There is no appreciable radiation between $145\ \mu\mu$ and $178\ \mu\mu$. The limits calculated in this way are probably less accurate than those given by Lyman.

In order to examine the effect produced by definite regions of the spectrum, the light from the source may be resolved by spectrum analysis, using either a diffraction grating or a prism. Convenient forms of a monochromatic illuminator for this purpose have been constructed by the firm of Adam Hilger (London).

Another method which is often useful in dealing with the ultra-violet portion of the spectrum is to make use of suitable screens which transmit a known region of the spectrum. Thus by using fluorite plates possessing different transparency limits Hughes \ddagger was able to show that the ionisation of air by ultra-violet light sets in at about $135\ \mu\mu$. Some years ago R. W. Wood \S suggested the use of the peculiar optical

* Lyman, *Nature*, **84**, p. 71, 1910.

\dagger Hughes, *Phil. Mag.*, **21**, pp. 393-404, 1911. \ddagger *Ibid.*, **25**, p. 685, 1913.

\S Wood, *Phil. Mag.*, **5**, pp. 257-263, 1903; *Physical Optics*, p. 15, 1911.

properties of nitroso-dimethyl-aniline in order to construct screens that should be transparent only to ultra-violet light.

J. Plotnikow * has described a number of filters suitable for use with a mercury vapour lamp in order to isolate definite regions in the spectrum.

The absorption by gases of the ultra-violet portion of the spectrum may also be utilised, as in the experiments of Palmer already described (p. 91). The coefficient of absorption in a number of gases of light which had passed through quartz windows has been measured by Varley.†

INFLUENCE OF THE INTENSITY OF THE LIGHT ON PHOTO-ELECTRIC PHENOMENA

THE NUMBER OF ELECTRONS

The number of electrons emitted is directly proportional to the intensity of the acting light. This fact, which is of fundamental importance in connection with the theory of photo-electric action, has been verified over a wide range. On this proportionality is based the use of a photo-electric cell in photometric measurements referred to in the introductory chapter. Elster and Geitel ‡ were the first to suggest the construction of a photo-electric photometer for measuring the intensity of sunlight, and in their first experiments they employed a surface of amalgamated zinc, which is sensitive to the shorter wave-lengths. The employment of such a surface was justified by experiments in which it was illuminated by light from a spark whose distance could be varied in a known manner ; good agreement was found between the observed results and those calculated on the assumption that the discharge of electricity was proportional to the intensity of the light.

Elster and Geitel § also record some data obtained with potassium cells that go to prove that the rate of discharge of electrons is directly proportional to the light intensity for

* Plotnikow, *Photochemische Versuchstechnik*, Leipzig, 1912.

† Varley, *Proc. Camb. Phil. Soc.*, **12**, pp. 510-516, 1904.

‡ Elster and Geitel, *Wied. Ann. d. Physik*, **48**, pp. 338-373, 1893.

§ Elster and Geitel, *Ann. der Physik*, **48**, p. 625, 1893.

small ranges of the latter. The walls of the cells were of glass, so that very little ultra-violet light penetrated to the potassium surface. The source of light was a petroleum lamp or an Auer gas burner.

The relation between the photo-electric current and the intensity of the light was investigated by Lenard,* who assumed that the intensity varied inversely as the square of the distance between the source and the detector. He obtained the following results :

$r.$	I.	E.	$E \div I.$
20.6	23.6	231.0	9.77
46.3	4.64	36.9	7.94
86.5	1.44	10.6	7.42

Lenard infers that E/I may be regarded as constant.

Indirect support was given to Lenard's conclusion by experiments carried out by Ladenburg † in which the angle of incidence of the light was varied by rotating the steel mirror upon which the light fell. If the value of the photo-electric current is divided by the cosine of the angle of incidence, the result is constant within the limits of experimental error. These experiments were carried out in a vacuum.

The relation between the intensity of the ultra-violet light falling on a negatively charged zinc plate and the quantity of electricity set free has been investigated by I. O. Griffith.‡ By varying the intensity of the light in the ratio 1 : 126 he found that the ratio of the photo-electric current to the light intensity did not remain constant, but increased with increase of intensity at a gradually increasing rate. These experiments, however, were not made in a high vacuum, but at a pressure of several millimetres of mercury.

* Lenard, *Ann. der Physik*, **8**, p. 154, 1902.

† Ladenburg, *Ann. d. Physik*, **12**, pp. 573-4, 1903.

‡ Griffith, *Phil. Mag.* (6), **14**, pp. 297-306, 1907.

The dependence of the photo-electric current on light intensity has been investigated by F. K. Richtmyer.* He measured the current from the surface of sodium contained in a glass cell. The cell was placed in a wooden box blackened on the inside, and the light from a 16 c.p. incandescent lamp fell upon it after passing one or more sheets of writing-paper. The intensity of the light incident on the cell was altered by varying the distance of the lamp and the number of layers of paper. A small current was observed even when the cell was in the dark. This was attributed to the fact that the sodium surface was highly electro-positive with regard to the second electrode, which was a platinum wire, and so produced a current over the slightly conducting surface of the glass walls of the cell. By charging the platinum wire connected to the sodium to a (negative) potential of about 3 volts (the contact potential difference between sodium and platinum) this effect could be eliminated, and the current obtained was due to the light alone.

The results of the first experiments are given in the table. They show that the photo-electric current from a sodium surface at zero potential is proportional to the light intensity for ranges of intensities from (approximately) 0.007 c.f. to 0.5 c.f.

Two thicknesses of Paper.

Lamp to Window.	Relative Light Intensity = I.	Deflection per second = \bar{E} .	$\frac{E}{I}$.
10.00 ft.	.0100	0.318 mm.	31.8
6.50	.0236	0.646	27.4
5.00	.0400	1.033	25.8
4.00	.0625	1.573	25.2
3.50	.0816	2.055	25.2
3.00	.111	2.682	24.2
2.75	.131	3.20	24.4
2.50	.160	3.93	24.6
2.25	.197	4.80	24.4

* Richtmyer, *Physical Review*, 29, pp. 71-80, 404-408, 1909.

One paper removed, increasing illumination 4.75 times.

Lamp to Window.	Relative Light Intensity = I.	Deflection per second = \bar{E} .	$\frac{E}{I}$.
4.00	.297	7.51	25.3
3.50	.387	9.79	25.3
2.50	.760	18.53	24.4

In a second investigation the observations are extended over a much larger range of light intensities. The current from the cell with a 12-volt battery was measured with a sensitive d'Arsonval galvanometer. The effects due to contact E.M.F. were far too small to interfere with these experiments. The source of light was an arc between solid carbons. For ten or fifteen seconds after lighting, the arc was found to be fairly steady, especially when the arc length was increased just beyond the hissing point. The intensity was varied by altering the distance of the arc from the cell. Up to the highest intensities employed (about 600 candle-feet) the photo-electric current was found to be directly proportional to the intensity of illumination.

Arc from Cell.	Illumination in Candle-feet = I.	Photo-electric Current, Amp. $\times 10^{-9}$ = \bar{E} .	$\frac{E}{I}$. <i>Result</i>
10.00 ft.	19	5.9	.310
8.00	30	8.7	.290
6.50	45	12.5	.278
5.50	63	16.4	.260
4.75	84	22.6	.269
4.00	118	31.4	.266
3.50	155	38.8	.250
3.00	210	52.6	.250
2.50	304	79.5	.258
2.25	375	97.5	.259
2.00	475	123.0	.260
1.75	620	160.0	.262

From these results we should conclude that the law of proportionality holds over an extremely wide range of light intensities, though some recent experiments by H. Dember* indicate a diminution in the photo-electric current in comparison with the light intensity, for large values of the latter. These experiments were carried out with two mercury vapour lamps and an arc lamp; the photo-electric current obtained when the cell was illuminated by two lamps simultaneously was smaller than the sum of the currents obtained with the same lamps used separately. The cells used were not exhausted to the highest attainable vacuum, though in one set of experiments with a potassium cell the pressure of the hydrogen was only 0.05 mm. of mercury. Further experiments with large light intensities seem to be required.

The variation of current with intensity of illumination has been considered in the course of a research by J. G. Kemp† on the sensibility of photo-electric cells with alkali metals in an atmosphere of hydrogen. Using a potassium cell in which the surface had been coloured bluish violet through the formation of a so-called hydride, Kemp found that the current was directly proportional to the intensity of illumination up to 1 candle-foot. The largest error observed amounted to about 7 per cent.; this error was probably due to want of steadiness in the current under the high voltages applied.

THE VELOCITY OF THE ELECTRONS

The velocity of emission of the electrons is independent of the intensity of the acting light. This was first shown by Lenard‡ from observations of the positive potential required to prevent the emission of electrons from the illuminated plate, or that required to prevent their reaching the receiving plate. A variation in the intensity of the light from a carbon arc in the ratio 70 to 1 produced a variation of less than 1 per cent. in the value of the positive potential. Similar results

* Dember, *Ber. Math.-Phys. Klasse Gesell. Wiss. Leipzig*, **64**, pp. 266-269, 1912.

† J. G. Kemp, *Phys. Rev.* (2), **1**, p. 285, 1913.

‡ Lenard, *Ann. d. Physik*, **8**, pp. 149-198, 1902.

were obtained with a zinc arc and with a spark as the source of light, though variations in the character of the source did produce variations in the initial velocity. Experiments were made with an aluminium plate and with a plate coated with lampblack.

Millikan and Winchester * confirmed Lenard's conclusion for the eleven metals they experimented upon in a high vacuum. The light intensity was varied both by changing the distance of the source and by altering the capacity in parallel with the spark, so as to make a spark of greater or less brilliancy. The final potential assumed remained the same, though the time required in assuming it varied as much as five or sixfold.

Similar results were obtained by Ladenburg † in the course of an investigation on the initial velocities of the electrons from platinum, copper, and zinc with monochromatic ultra-violet light. The intensity of the light was changed by altering the width of the slit of the spectrometer. A mercury vapour lamp of quartz was used as the source of light. The result has also been verified by Mohlin.‡

Experiments of Elster and Geitel § with a surface of sodium-potassium alloy showed that the positive potential acquired by the illuminated surface remained unchanged when the intensity of the light was diminished by closing an iris diaphragm, although the time required to reach a maximum value increased. To obtain reliable results in such experiments great precautions must be taken to secure good insulation, as otherwise the potential reached depends not only on the velocity but also on the number of the electrons emitted.

In J. R. Wright's || experiments with an aluminium plate in a high vacuum it is shown incidentally that the positive potential is quite independent of the intensity of the light. Very powerful sparks between electrodes of zinc, cadmium, and iron served as the source of light. While the relative

* Millikan and Winchester, *Phil. Mag.*, (6), **14**, p. 201, 1907.

† Ladenburg, *Deutsch. Phys. Gesell. Verh.*, **9**, p. 508, 1907.

‡ Mohlin, *Akad. Abhandl.*, Upsala, 1907.

§ Elster and Geitel, *Phys. Zeit.*, **10**, pp. 457-465, 1909.

|| J. R. Wright, *Phys. Rev.*, **33**, pp. 43-52, 1911.

intensities of the light for wave-length 2166 were approximately as 10 : 12 : 100, the widest variation of the positive potentials from the mean is less than 0.5 per cent.

In view of these results the conclusion that the maximum velocity of emission is independent of the intensity of the light may be regarded as well established.

CHAPTER X

THE INFLUENCE OF THE CHARACTER OF THE LIGHT ON THE PHOTO-ELECTRIC DISCHARGE (continued)

THE INFLUENCE OF THE PLANE OF POLARISATION AND OF THE WAVE-LENGTH OF THE LIGHT ON PHOTO-ELECTRIC PHENOMENA

WITH a view to the right understanding of photo-electric action, it is of great importance to know how the phenomena are affected by alterations in the quality of the exciting light. We may alter the quality of the light by changing its state of polarisation and also by varying the wave-length. It will be convenient to consider the effects produced by both these variations in a single chapter, since they are found to be, to a certain extent, interdependent. The important work of Pohl and Pringsheim has led to the conclusion that we must distinguish between two separate actions, by which electrons can be released, the "normal" and the "selective" photo-electric effect. This distinction has been rendered possible only by examining the results of varying both the plane of polarisation and the wave-length of the incident light. It will, however, be convenient to describe first of all some of the earlier results in which plane-polarised light was employed, without special attention being directed to the wave-length made use of.

INFLUENCE OF THE PLANE OF POLARISATION OF THE LIGHT

In his original paper describing the effect of ultra-violet light on the length of the spark discharge, after showing that the action can be refracted according to the laws of light, Hertz says: "I have not been able to decide whether any double refraction of the action takes place." In a supplementary note (1891) he remarks: "Somewhat later I suc-

ceeded in this. I had hoped to observe an influence of the state of polarisation of the light upon the action, but was not able to detect anything of the kind."

Elster and Geitel* were the first to show an effect due to the polarisation of the incident light. The sensitive substance was the liquid alloy of sodium and potassium which responds to light from the visible spectrum. The photo-electric cell was included in a circuit containing a galvanometer and a pile of 250 volts. Polarised white light was incident at an angle of 45° . They found that the photo-electric current was a maximum when the plane of polarisation was perpendicular to the plane of incidence, and a minimum when these planes were parallel. In other words, the maximum value of the photo-electric current corresponds to the case in which the electric vector in the wave front has a component at right angles to the surface of the metal. The ratio of the maximum to the minimum was about 10 to 1. The intensity of the photo-electric current could be expressed by the equation $I = A \cos^2 \alpha + B \sin^2 \alpha$, where α is the angle between the planes of incidence and polarisation.

The following table shows how the effect depends on the angle of incidence.

Photo-electric Current from Sodium-potassium Alloy exposed to Plane Polarised White Light

Angle of incidence.	Light polarised at right angles to the plane of incidence.	Light polarised in the plane of incidence.
0°	2.8	...
3°	...	2.8
10°	5.2	2.78
20°	11.2	2.87
30°	17.4	2.65
40°	23.4	2.24
50°	27.0	1.80
60°	28.7	1.51
70°	23.8	1.01
80°	11.0	0.33

* Elster and Geitel, *Wied. Ann. d. Physik*, **52**, p. 540, 1894; **55**, p. 684, 1895; **61**, p. 445, 1897.

At perpendicular incidence the two currents are necessarily the same, but for all other angles the effect due to light polarised at right angles to the plane of incidence is greater than that due to light polarised in the plane of incidence. In the former case the effect reaches a maximum for an angle of about 60° .

Amalgams of the metals rubidium, caesium, potassium, and sodium show similar behaviour.

These experiments were carried out, not in the highest vacuum, but at the "critical" pressure (about $\frac{1}{3}$ mm.) corresponding to maximum photo-electric current.

The result of the observations may be summarised by saying that the photo-electric current is approximately proportional to the amount of light absorbed by the illuminated surface, but the factor of proportionality is greater for light polarised at right angles to the plane of incidence than for light polarised in the plane of incidence. In the case of the Na-K alloy the two factors are in the ratio 30 to 1.

In a later investigation, Elster and Geitel* have further studied the influence of the state of polarisation of the exciting light, with special reference to the dependence of the number and the velocity of the emitted electrons on the position of the plane of polarisation with regard to the plane of incidence. An extremely high vacuum was obtained by absorbing the residual gases in the cell by glowing calcium, according to the method worked out by F. Soddy. They arrive at the following conclusions in the case of the liquid alloy of sodium and potassium :

1. Light polarised perpendicularly to the plane of incidence causes the emission of more (up to 50 times as many) negative electrons than light polarised parallel to that plane.
2. The maximum velocities of the electrons are about the same for both positions of the plane of polarisation.
3. The number of electrons with a velocity less than the maximum is (with reference to equal total numbers) greater if the light is polarised perpendicularly to the plane of incidence than if the plane of polarisation is parallel to that plane.

* Elster and Geitel, *Phys. Zeitschr.*, **10**, pp. 457-465, 1909.

In interpreting these results we must remember that, when the light is polarised perpendicularly to the plane of incidence, the electric vector in the light wave is vibrating parallel to the plane of incidence. It appears, then, that when the electric vector has a component perpendicular to the surface of the alkali metal it is able to release more electrons than when it is parallel to the surface.

Lenard,* and subsequently Ladenburg,† found that when the test was carried out with ultra-violet light on metals in a good vacuum the position of the plane of polarisation is without influence. This may be explained, according to Ladenburg, by supposing that the ultra-violet light penetrates some considerable distance into the metal. Thus in the case of nickel he estimated that the light penetrated to a depth of 8 wave-lengths. Very much smaller estimates (about $50 \mu\mu$) of the depth of penetration of ultra-violet light in platinum have been made by Robinson,‡ and by Partzsch and Hallwachs.§

The dependence of the photo-electric effect on the polarisation of the light in the case of solid metals has been shown to exist by R. Pohl.|| With mirrors of platinum and copper the number of electrons emitted depends on the azimuth and the angle of incidence of the polarised ultra-violet light. The same is true for fluid mercury. This can be explained by a proportionality between the number of electrons emitted and the quantity of light absorbed in each case. The proportionality factor is the same whether the light is polarised parallel or at right angles to the plane of incidence. This is in marked contrast with the behaviour of the alkalis, where an extraordinary increase in the current (as much as fiftyfold) is found when the electric vector has a component perpendicular to the surface. With ultra-violet light the alkalis behave like

* Lenard, *Ann. d. Physik*, **8**, p. 150, 1902.

† Ladenburg, *Ann. d. Physik*, **12**, p. 574, 1903.

‡ Robinson, *Phil. Mag.*, **25**, p. 131, 1913.

§ Partzsch and Hallwachs, *Ber. Math.-Phys. Klasse Konig. Sachsichen Gesell. Wiss.*, **64**, pp. 164, 165, 1912.

|| Pohl, *Phys. Zeit.*, **10**, pp. 542-543, 1909; *Deutsch. Phys. Gesell. Verh.*, **11**, pp. 339-359, 609-616, 1909.

other metals. We shall return to this question in discussing the influence of wave-length.

The influence of the plane of polarisation of the incident light on the positive potential acquired by a metal has been examined by Jakob Kunz * in the case of the liquid alloy of sodium and potassium. When the light was polarised at right angles to the plane of incidence, the positive potential was 1.10 volts. As the polarising Nicol prism is rotated the positive potential diminishes, and when it is turned through a right angle the positive potential is only 0.723 volts. Thus the positive potential decreases 34.3 per cent. in going from one position to the other. This result is at variance with that obtained by Elster and Geitel for the same alloy, and with that obtained by Pohl † for a solid metal surface, for these experimenters found the maximum velocity of emission of electrons to be independent of the position of the plane of polarisation.

INFLUENCE OF WAVE-LENGTH ON PHOTO-ELECTRIC PHENOMENA

We now consider the influence of the wave-length or frequency of the light. We must inquire how the number of electrons emitted in unit time—that is, the photo-electric current—depends on the wave-length, and secondly how the velocity of emission varies with the wave-length. We have seen that the increase in the length of the spark discharge caused by illuminating the spark-gap was traced by Hertz to light beyond the violet of the visible spectrum. Ultra-violet light is also most active in bringing about the discharge of negative electricity observed by Hallwachs. Elster and Geitel ‡ have shown that ordinary daylight is capable of producing this effect in the case of the more electro-positive metals. Using a petroleum lamp as a source of white light, and employing various coloured filters, they obtained the results given in the following table :

* J. Kunz, *Phys. Rev.*, **29**, pp. 174-176, 1909.

† Pohl, *Verh. Deutsch. Phys. Gesell.*, **11**, pp. 339-359, 1909.

‡ Elster and Geitel, *Ann. d. Physik*, **52**, p. 438, 1894.

Colour of Light.	Rate of Leak of Negative Electricity.		
	Na	K	Rb
White . . .	21.0	53.1	537.0
Blue . . .	7.8	30.3	86.8
White . . .	22.6	52.9	527.7
Yellow . . .	8.2	3.5	339.7
White . . .	21.9	53.9	552.3
Orange . . .	3.1	2.2	182.0
White . . .	21.9	52.9	527.7
Red . . .	0.2	0.1	21.0

Rubidium, the most electro-positive metal, is far more active than sodium or potassium with white light, and potassium is more active than sodium. In the case of sodium and rubidium the maximum effect would appear to be produced by yellow light, while with potassium blue light is more effective. Rubidium is active even under the influence of the long waves at the red end of the spectrum, indeed a red-hot glass rod is said to be sufficient to discharge negative electricity from this metal.

These effects are attributed to the strong absorption of light of particular wave-lengths by the substances under consideration.

J. J. Thomson* found that a positively charged metal plate placed opposite to a surface of sodium-potassium alloy or of rubidium lost its charge even in the dark. Thomson himself at first attributed this to a radio-active process, but, according to E. Müller,† it is to be explained by the action of infra-red radiation, which produces no effect on the eye, though it is able to produce photo-electric emission from the alkali metal.

Hallwachs‡ proved that the violet and ultra-violet radiations were most effective in bringing about a discharge from metal plates. For plates of copper oxide the effect was greatest for the light from the arc *between* the carbons.

* J. J. Thomson, *Phil. Mag.*, **10**, p. 584, 1905.

† E. Müller, *Deutsch. Phys. Gesell. Verh.*, **11**, p. 72, 1909.

‡ Hallwachs, *Ann. d. Physik*, **33**, pp. 301-312, 1888.

M. Branley * showed that freshly-polished metals, notably aluminium, are particularly sensitive; daylight produces the discharge; the action still takes place when the light has passed through yellow glass, but red glass stops it entirely.

Elster and Geitel † observed photo-electric action in sunlight in the case of the metals aluminium, magnesium, and zinc, but the active rays were almost completely absorbed by transmission through glass. Fluor-spar was also active in sunlight, and in this case ultra-violet light was *not* the most efficient.

Buisson ‡ found sunlight a convenient source of light in his experiments with amalgamated and polished zinc and aluminium.

W. Rudolph § states that aluminium certainly, and in all probability a number of other metals also, show the Hertz-Hallwachs effect with visible light.

The results so far described are qualitative rather than quantitative, for until we know the amount of energy associated with the different parts of the spectrum of the light employed, we cannot strictly compare the effects of light of different refrangibilities.

Quantitative experiments have been made by E. Ladenburg. || A mercury vapour lamp was used as a source of light. The spectrum of the light was given by a spectrometer with quartz-fluor-spar lenses and a fluor-spar prism. The energy in different parts of the spectrum was measured by a thermopile. The photo-electric current for the metals Cu, Pt, Zn was measured with a galvanometer, and was found to be a maximum for a wave-length 212–218 $\mu\mu$. For equal light intensities the photo-electric effect increased continuously as the wave-length diminished. In the accompanying figure the ordinates of the curve marked E_1 represent the saturation current from the illuminated platinum plate, the ordinates of

* M. Branley, *Journal de Physique*, **3** (11); p. 300, 1893.

† Elster and Geitel, *Nature*, **50**, p. 451, 1894.

‡ Buisson, *Annal. Chim. Phys.*, **24**, pp. 320–398, 1901.

§ W. Rudolph, *Ann. d. Physik*, **20**, pp. 111–124, 1909.

|| E. Ladenburg, *Phys. Zeitschr.*, **8**, pp. 590–594, 1907; *Deutsch. Phys. Gesell. Verh.*, **9**, pp. 504–514, 1907.

the curve E_2 represent the energy of the *incident* light,* while the ordinates of the third curve give the ratio (E_1/E_2) of these two quantities expressed as a function of the wave-length. The final curves, giving this ratio for copper and zinc, were

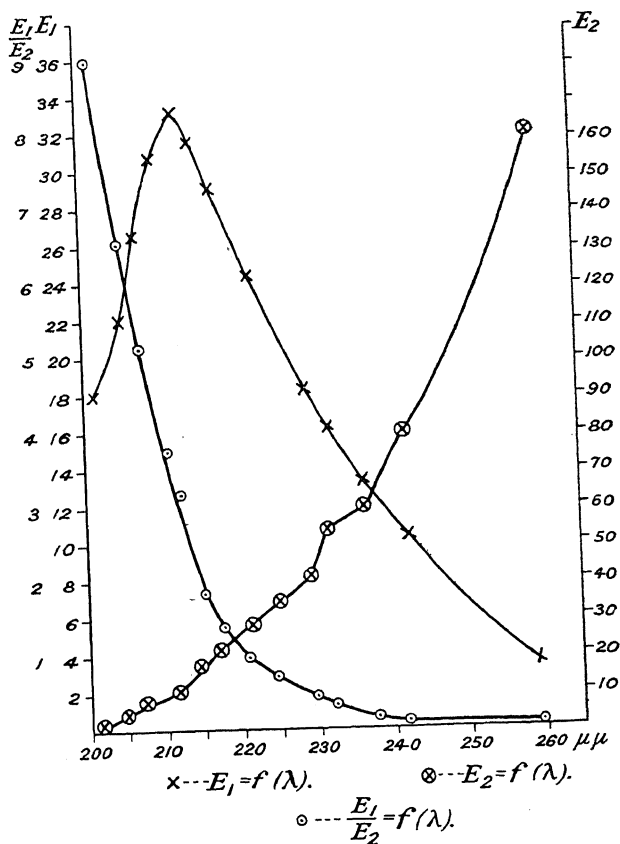


FIG. 27

very similar to that here shown for platinum. Results of the same kind have been obtained by Mohlin.†

The ratio of the photo-electric activity to the energy of

* Information is to be desired as to the energy absorbed by the metal surface, and as to the fraction of the absorbed energy that is directly related to the photo-electric effect. See R. Ladenburg, *Jahrbuch der Radioaktivität*, 6, p. 446, 1909.

† Mohlin, *Akad. Abhandl.*, Upsala, 1907.

the incident light (E_1/E_2) has been termed the specific photo-electric activity.

Since all bodies which have been tested in ultra-violet light show increasing activity as the wave-length diminishes, it is of interest to know whether the alkali metals behave in similar fashion. The experiments of Elster and Geitel would seem to indicate that these metals show a maximum specific photo-electric activity for rays of the visible spectrum. J. Braun* found a maximum in the case of potassium at $440 \mu\mu$. In these experiments the metal was contained in cells of glass, so that only rays that have escaped absorption by glass can take effect. An investigation to determine the photo-electric activity of potassium as a function of the wave-length has been carried out by W. Hallwachs.† The potassium was illuminated through a quartz window by light from a mercury vapour lamp or from an arc. By means of a quartz-fluorspar achromatic lens and a quartz prism, a real spectrum was produced on a fluorescent screen, and selected lines were then allowed to enter the cell. The energy measurements were carried out by a thermo-electric method.

The results of the measurements are given in the following table, being referred to the line $436 \mu\mu$ as a standard :

Wave-length . . .	578	546	436	406	365	313	254	217
Photo-electric activity	0.032	0.083	1.00	0.79	2.18	3.01	1.98	3.90
Energy	1.16	1.69	1.00	0.67	1.19	0.90	0.38	0.55
Specific photo-electric activity	0.027	0.049	1.00	1.18	1.83	3.34	5.2	7.1

According to these results potassium falls into line with the other metals, the specific photo-electric activity increasing as the wave-length gets less. There is no evidence of a maximum in the visible spectrum.

The disagreement between the results of Elster and Geitel

* J. Braun, *Diss. Bonn*, 1906.

† Hallwachs, *Ann. der Physik*, 4, 30, pp. 593-597, 1909.

and J. Braun on the one hand, and those of Hallwachs on the other, has received an explanation through the work of Pohl and Pringsheim.* These authors show that the photo-electric activity depends on the angle at which the light is incident on the surface, and on the orientation of the plane of polarisation. When the light falls normally on the surface as in the experiments of Hallwachs, the electric vector is parallel to the surface, and the photo-electric activity of a K-Na alloy increases continuously as the wave-length decreases. But when the light is incident at an angle with the normal, the electric vector which is parallel to the plane of incidence produces a maximum effect for a particular wave-length ($\lambda = 400 \mu\mu$). The proportionality factor between light absorption and photo-current is only independent of the angle of incidence ϕ for an electric vector ($E \perp$) vibrating at right angles to the plane of incidence, while for an electric vector ($E \parallel$) parallel to the plane of incidence it varies very much with ϕ . Further, the factor varies greatly with the wave-length.

The way in which the specific photo-electric activity varies with the wave-length when the angle of incidence is 60° is shown in the following diagram (Fig. 28).

The electric vector vibrating parallel to the plane of incidence produces a maximum effect for a wave-length $400 \mu\mu$, while the electric vector which is parallel to the metal surface produces a smaller effect, which increases as the wave-length diminishes. The maximum in the first curve is taken to indicate a resonance phenomenon.

It follows from these experiments that for Na, K, Rb, and NaK there is a certain region of wave-lengths for which there is a very great difference between the current produced by E perpendicular and E parallel to the plane of incidence. The wave-length corresponding to the maximum difference may be called the critical wave-length; it is the wave-length that makes the photo-electric activity due to the electric vector parallel to the plane of incidence a maximum. The

* Pohl and Pringsheim, *Deutsch. Phys. Gesell., Verh.*, **12**, pp. 215-228, 349-360, 1910.

maxima are approximately at $\lambda=480 \mu\mu$ for rubidium, $435 \mu\mu$ for potassium, $340 \mu\mu$ for sodium, and $280 \mu\mu$ for lithium. For a potassium-sodium alloy containing 69.4 per cent. potassium, the maximum is at about $390 \mu\mu$. In the case of the amalgams of potassium and sodium no critical wave-length was found. This indicates that we have to do with a resonance phenomenon connected with the molecular binding of the alkali atoms.

Pohl and Pringsheim distinguish between two actions which they describe as the "selective" and the "normal"

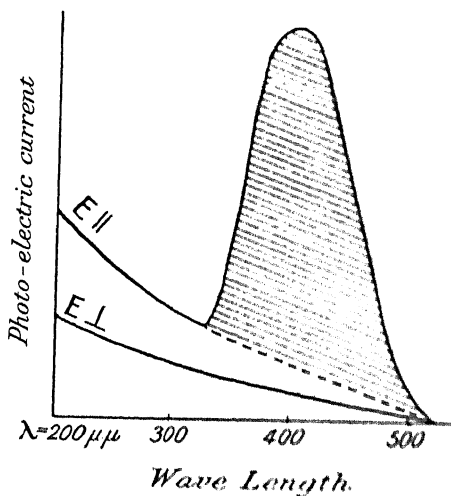


FIG. 28

photo-effect. It is the former effect which gives rise to the maximum in the curve for the specific photo-electric activity, when the electric vector is parallel to the plane of incidence. The normal effect would give increasing activity with diminishing wave-length for all directions of the electric vector. This is indicated by the dotted line in the diagram.

A selective effect has been found with barium which shows a maximum at $\lambda=280 \mu\mu$, but the other metals (Pt, Cu, Hg, Pb, Tl, Sn, Cd, Bi) examined showed only the normal effect.*

The difference between the selective and the normal effect

* *Deutsch. Phys. Gesell. Verh.*, **13**, pp. 474-481, 1911.

may be illustrated, according to Pohl, by the mechanical analogy of a float which is caused to rise and fall by a progressive train of water waves. Two cases are then possible. In the first place the float may be attached to a fixed point by an elastic connection, as, for instance, by a spiral spring. By the action of the advancing water-waves the float is set in vibration, and, if the period of vibration of the water-waves happens to be in agreement with the natural period of the float, the amplitude of the vibration may become so great that the spring breaks. The float flies off, not in any random direction, but in a direction in the plane of vibration of the water particles and perpendicular to the direction of propagation. In the second place a float without any elastic connection may go up and down on the water-waves, and by means of some simple mechanism, such as a balance wheel, stretch a spring, and the energy of this stretched spring may serve to do a certain amount of work, as in projecting a ball or even the float itself in any desired direction, which need not lie in the direction of vibration of the water particles or be perpendicular to the direction of propagation. The first case may be taken to correspond with the selective, the second with the normal, photo-electric emission.

Experiments just completed by Compton and Richardson * have carried the investigation of the effect of the wave-length on the number of electrons emitted further into the ultra-violet than ever before (to $200\ \mu\mu$). The curves for sodium show *two* maxima instead of only one maximum, and the conclusion is drawn that the normal photo-electric effect reaches a maximum similar to that reached by the selective effect, but farther out in the ultra-violet. The photo-electric sensitivity is supposed by the authors to be the same function of the frequency for all metals, but for the electronegative metals the curve is shifted bodily towards the region of short wave-lengths.

* Compton and Richardson, *Phil. Mag.*, **26**, pp. 549-567, 1913.

THE VELOCITY OF THE ELECTRONS AND THE FREQUENCY OF VIBRATION OF THE LIGHT

When an insulated body is illuminated it acquires a positive potential which rises to a definite maximum value, dependent on the character of the light. As Lenard has pointed out, this positive potential may be regarded as a measure of the maximum velocity with which electrons are emitted under the influence of the light. For if V denote this potential—that is, the potential which is just sufficient to prevent the discharge of electricity from the body— Ve would represent the work that would have to be done to remove an electron, and we should have

$$Ve = \frac{1}{2}mv^2$$

Thus the positive potential V is directly proportional to v , the maximum velocity with which an electron is projected.

Lenard * concluded from his experiments that, though the positive potential was independent of the intensity of the light, it did vary with the character of the source. With a zinc arc large initial velocities are represented in very much smaller proportion than with a carbon arc. The spark as a source comes between the two. This refers to a lampblack surface; for an aluminium plate the differences are not so great.

Ladenburg,† experimenting with the three metals copper, platinum, and zinc, found that the initial velocities of the electrons increased with decreasing wave-length. He concluded that the velocity was proportional to the frequency of the incident light. The results are summarised in the following table:

Frequency.	Wave-length.	Positive potential in volts.		
$\nu \times 10^{-15}$	$\mu\mu$	Platinum.	Copper.	Zinc.
1.15	260	1.075	1.01	0.685
1.24	242	1.28	1.16	0.79
1.31	229	1.49	1.33	0.95
1.375	218	1.60	1.46	1.0
1.43	210	1.76	1.55	1.07
1.49	201	1.86	1.69	1.12

* Lenard, *Ann. d. Physik*, **8**, pp. 149–198, 1902.

† Ladenburg, *Phys. Zeitschr.*, **8**, pp. 590–594, 1907.

Ladenburg and Markau * obtained the velocity distribution curves from which the number of electrons with any assigned velocity could be determined. For a given region of the spectrum the velocities were found to be nearly in accordance with Maxwell's law of distribution. For light of wave-length $260 \mu\mu$ the limits of velocity are equivalent to 0.4 and 1.9 volts. The range of wave-lengths used was from $270 \mu\mu$ to $200 \mu\mu$.

Ladenburg's results were examined by A. Joffé,† who pointed out that the conclusion drawn from them was a

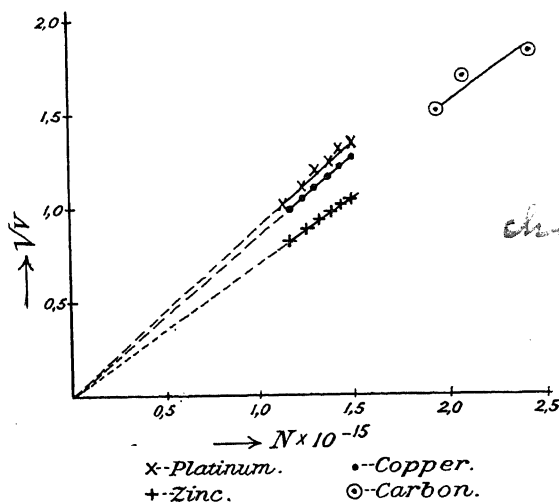


FIG. 29

doubtful one. According to Ladenburg the initial velocity was proportional to the frequency ($v = kv$). Joffé showed that the results agreed at least equally well with the conclusion that the positive potential (or the square of the velocity) was proportional to the frequency, or more exactly $V = k(v - v_0)$. This is due to the fact that the experimental results refer to a very short range of wave-lengths, and it is difficult to decide whether they fall on a straight line or on a short piece of a parabola at some distance from the vertex. The two laws are best illustrated graphically. In the first diagram (Fig. 29)

* Ladenburg and Markau, *Phys. Zeitschr.*, 9, p. 251, 1909; *Deutsch. Phys. Gesell. Verh.*, 10, pp. 562-577, 1908.

† Joffé, *Ann. d. Physik*, 24, p. 939, 1907.

Curve I: ...

the square root of the positive potential is plotted against the frequency, and it is seen that the points for a given metal lie on a straight line passing through the origin. In the second diagram (Fig. 30) the positive potential is plotted against the

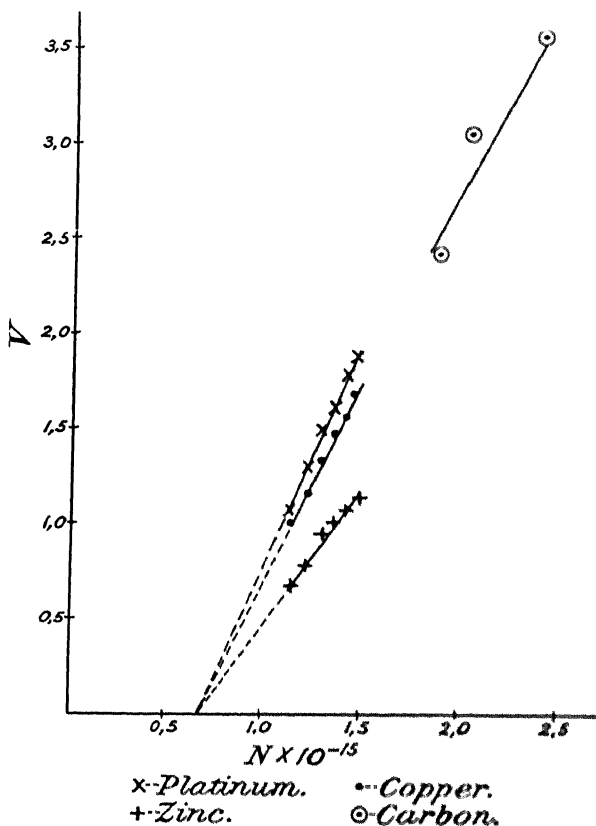


FIG. 30

frequency, and the observed points for a given metal lie on a straight line which does not pass through the origin.

A. W. Hull * has made measurements of the initial velocities of the electrons liberated from carbon by light of short wavelength (between $171 \mu\mu$ and $123 \mu\mu$). He finds that the maximum initial velocity is proportional to the frequency of

* Hull, *Amer. Journ. Sci.*, **28**, pp. 251-259, 1909; *Phys. Zeit.*, **10**, pp. 537-542, 1909.

vibration of the light, so far as it is possible to infer a result when regard is paid to the accuracy with which this part of the spectrum is known. Three regions were examined by means of absorption screens, and the assumption was made that the maximum velocities are due to the shortest wave-length made use of. If these results are examined in the same way as Ladenburg's (Figs. 29 and 30), we find that they satisfy the second law equally well.

The velocities of the electrons emitted from an equimolecular liquid alloy of sodium and potassium have been studied by Jakob Kunz.* He found that the potential difference between the electrodes was independent of the intensity of the light and equivalent to 1.12 volts. He also measured the potential due to light of various wave-lengths between $592\ \mu\mu$ and $420\ \mu\mu$, using an arc lamp as the source of light. Except at the red end of the spectrum the potential difference appears to be inversely proportional to the wave-length—that is, the kinetic energy of the electrons is proportional to the frequency. This does not hold good for wave-lengths greater than $520\ \mu\mu$, and the author suggests that the divergence from proportionality may be due to a heating effect. Later experiments by Kunz † indicate a maximum value of the positive potential in the red end of the spectrum. The sodium-potassium alloy shows a maximum at wave-length $618\ \mu\mu$. In this region of the spectrum the positive potential depends on the intensity of the light, while towards the violet end of the spectrum the positive potential is not much affected by the intensity. Experiments with sodium-potassium alloy and with caesium, using the resolved light of a spark between cadmium or zinc terminals, prove that the positive potential increases with increasing frequency. The author now concludes that the positive potential is proportional to the square of the frequency of the light. It is pointed out that the surface conditions play a very important part in the results obtained; it is very difficult to prepare the metal with the same photo-electric properties twice in succession.

* J. Kunz, *Phys. Rev.*, **29**, pp. 212–228, 1909.

† *Ibid.*, **33**, pp. 208–214, 1911.

Some very remarkable results have been obtained by Professor R. A. Millikan* and his fellow-workers in the University of Chicago by using a powerful spark as the source of light instead of a quartz mercury lamp. The positive potentials acquired by metals illuminated by such a source were greatly in excess of those obtained by other observers. Although experiments were carried out which seemed to show that the high potentials were due to the light itself and not to secondary effects, later experiments proved that the results were to be attributed to imperfect screening from electromagnetic waves.

It is open to question how far such an effect may have had an influence in some earlier experiments of J. R. Wright,† in which the positive potential of an aluminium plate was measured for definite wave-lengths in the region extending from λ 2878 to λ 2073. The results obtained are not in agreement with those of other observers in that they show an apparent maximum for the positive potential for a particular wave-length (λ 2166).

An important investigation of the emission velocities of photo-electrons has been carried out by A. L. Hughes.‡ The metal surfaces used were prepared by distillation *in vacuo*, as it was found that in this way consistent results could be obtained. The surface so prepared is probably free from surface films, which are almost certainly present when a metal plate is polished or when an electric discharge is passed, using the plate as an electrode. A Hilger quartz spectrograph was used as a monochromator. It was found that this did not isolate the wave-lengths perfectly, and special precautions had to be taken to cut off the scattered light of short wave-length when working with the longer wave-lengths. The mercury arc in quartz glass was used as the source of light.

The apparatus is shown approximately to scale in the diagram (Fig. 31). The electrical capacity is made very small

* R. A. Millikan, *Phys. Rev.*, **35**, p. 74, 1912; Millikan and Wright, *Phys. Rev.*, **34**, p. 68, 1912; Millikan, *Phys. Rev.* (2), **1**, pp. 73-75, 1913.

† J. R. Wright, *Phys. Rev.*, **33**, pp. 43-52, 1911.

‡ A. L. Hughes, *Phil. Trans. Roy. Soc.*, **212**, pp. 205-226, 1912.

on account of the feebleness of the monochromatic light. The light falls on a disk, N, of nickel, 3 cm. in diameter. In the

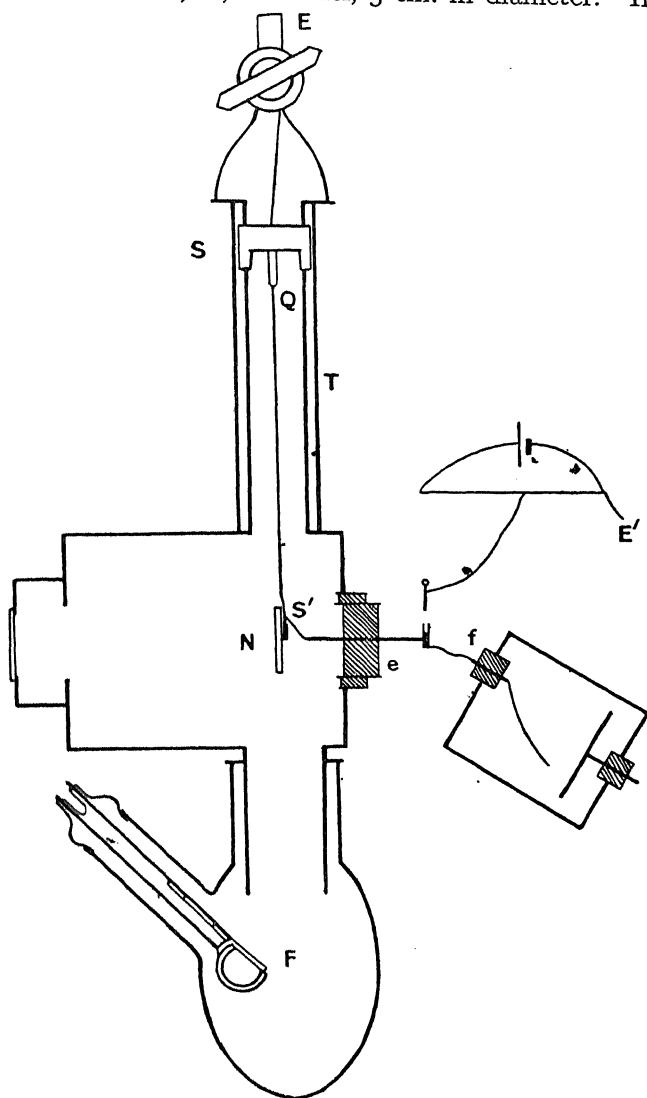


FIG. 31

position shown the disk is put in contact with the tilted electro-scope by means of the spring S' . The disk is suspended by a fine wire from the quartz rod Q , which is attached to the

slide S. This runs in grooves in the tube T. The system can be raised or lowered by a silk thread attached to the winch E, which is a glass tap with a groove cut round the barrel. In order to coat the plate N with metal it is lowered till it is near the little furnace F. This is a quartz ignition spoon into which fits a thin quartz cup containing the metal. Between the cup and the quartz spoon there is a thin sheet of Pt or Ni, which can be heated to redness by a current. The apparatus was exhausted by a Toepler pump to a pressure of .01 mm., and finally by a tube containing charcoal cooled in liquid air.

Experiments made with this apparatus, using surfaces of pure distilled metal, proved that the maximum energy of emission, and not the maximum velocity, can be expressed as a linear function of the frequency of the incident light. The proof is based mainly on experiments made with wavelengths λ 2537, λ 2257, and λ 1849. One set of results obtained from a surface of distilled cadmium may be quoted in illustration.

Cadmium.

Wave-length λ .	Frequency $\nu \times 10^{-12}$.	Experimental Velocities in volts.	Calculated Velocities.	
			$V = h\nu - V_0$	$\sqrt{V} = \sqrt{h\nu - c}$
1849	1623	2.480	[2.480]	[2.480]
2257	2329	1.427	1.424	1.339
2537	1182	0.897	[0.897]	[0.897]
2967	1010	0.148	0.286	0.495
3126	960	Small	0.101	0.398
3340	898	No effect	(-0.12)	0.293

$$V_0 = 3.347 \text{ volts; } h = 3.590 \times 10^{-15}.$$

The velocity predicted by the energy law for λ 2257 is in much better agreement with the experimental value than that predicted by Ladenburg's law. The experimental values for λ 2967 and λ 3126 are lower than the theoretical values on account of the action of the earth's magnetic field. Laden-

burg's law would indicate an emission of electrons down to λ 4000. Actually the emission ceases between λ 3126 and λ 3340 in accord with the energy law.

Similar results were obtained with other metals, showing clearly that it is the energy and not the velocity of the electrons that is a linear function of the frequency of the light. The positive potential V , in volts, is connected with the frequency ν by the formula $V = k\nu - V_0$. Thus the emission of photo-electrons should cease below a certain definite frequency, determined by $V_0 = k\nu_0$. This was borne out by experiment.

The values of the constants found by Hughes for a number of metal surfaces formed by distillation are given in the table.

Element.	k	V_0	$\nu_0 \times 10^{-13}$ (calculated).	λ_0 in $\mu\mu$ (calculated).
		volts		
Ca . . .	3.17×10^{-15}	2.57	81.1	370
Mg . . .	3.39	3.08	90.9	330
Cd . . .	3.66	3.49	95.3	315
Zn . . .	3.79	3.77	99.5	302
Pb . . .	3.55	3.42	96.3	311
Bi . . .	3.63	3.37	92.8	323
Sb . . .	3.69	3.60	99.8	800
As . . .	≈ 3.7	≈ 4.5	$\approx 122.$	≈ 247
Se	≈ 4.8
O ₂	≈ 8.0

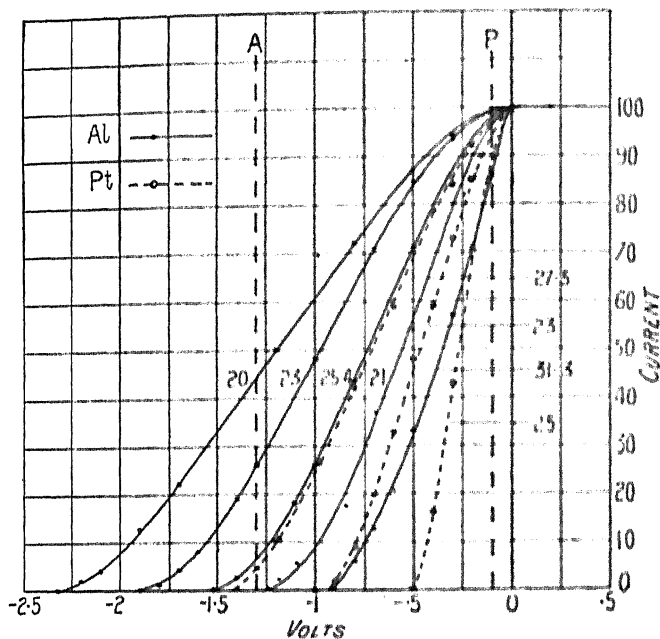
The values of k and V_0 for elements of the same valency change regularly with the atomic volume.

Curves showing the distribution of velocities have been obtained by Richardson and Compton* for the metals platinum, copper, bismuth, tin, zinc, aluminium, and magnesium. The points of special interest in the experimental work are as follows: (1) the contact difference of potential between the emitting and receiving electrodes is allowed for; (2) an improved monochromatic ultra-violet illuminator by Adam Hilger Ltd., is made use of; (3) the peculiar form of the photo-electrical cell practically eliminates electron reflection without the use of a screen and an auxiliary field,

* Richardson and Compton, *Phil. Mag.*, **24**, pp. 575-594, 1912.

and at the same time it enables the distribution of total kinetic energy to be measured instead of simply the distribution of the velocity component normal to the emitting electrode.

The electrode consists of a strip of metal foil about 1 mm. wide and 5 mm. long placed at the centre of a spherical glass bulb of 7.5 cm. diameter. This bulb is silvered on its inner surface, which acts as the receiving electrode. The image of



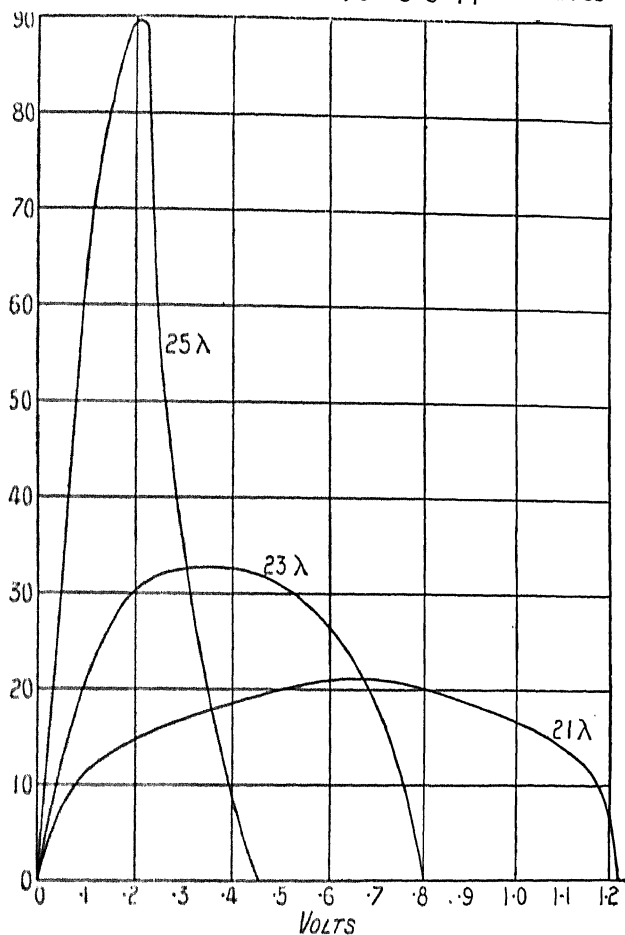
Messrs. Taylor & Francis, Publishers *Philosophical Magazine*.

FIG. 32

the slit of the monochromator is focussed on the metal strip for the particular wave-length to be examined. The electric field is approximately radial, and the area of the emitting electrode is very small compared with the area of the receiving electrode.

The dotted lines in Fig. 32 show graphically the results for platinum, the photo-electric current reduced to a scale of 100 for the maximum being plotted against the P.D. The vertical line P indicates the amount of lateral shift that had to be given to the diagram to correct for the contact

difference of potential between platinum and silver. The line A is the corresponding line for aluminium. The continuous curves represent the results obtained with aluminium for wave-lengths 200, 230, 254, 275, 313 $\mu\mu$. Curves of the



Messrs. Taylor & Francis, Publishers Philosophical Magazine.

FIG. 33

same character were obtained with the metals zinc, bismuth, magnesium, tin, and copper. If we plot the slope of these curves against the potential difference, we obtain what may be called the differential curves. These are shown for platinum in the annexed figure (Fig. 33). We can then

obtain the relative number of electrons which are emitted with any given energy. For wave-length 25×10^8 cm. the number emitted with an energy corresponding to 0.2 volt is to the number corresponding to 0.1 volt as the ordinate at 0.2 volt is to the ordinate at 0.1 volt, or as 90 is to 65.

The following conclusions are drawn from a study of these curves :

1. The maximum energy, expressed in volts, is a linear function of the frequency of the exciting light.

2. The curves appear to be almost symmetrical with respect to their maximum ordinates. This shows that, if the maximum energy is a linear function of the frequency, the average energy, which is equal within the limits of experimental error to the most probable energy, also bears a linear relation to the frequency.

3. The curves intersect the voltage axis at finite angles both at the end which corresponds to zero energy and at the end which corresponds to the maximum energy.

4. If the wave-length is increased to a certain value, the distribution of velocity curve will degenerate into a straight line coincident with the current axis. This is the longest wave-length that will produce any photo-electric effect from the metal under investigation, and the corresponding electrons are emitted with zero velocity.

Reviewing the results obtained by various experimenters as to the relation between the velocity of emission of the electrons and the frequency of the light, we must conclude that the velocity increases with the frequency, and that the maximum kinetic energy (which is proportional to the positive potential) is a linear function of the frequency. With the notation already used, V being the positive potential *in volts*,

$$V = k(\nu - \nu_0);$$

or, if T_m is the maximum kinetic energy and k_m is a new constant,

$$T_m = \frac{1}{2}mv^2 = \frac{V_e}{300} = k_m(\nu - \nu_0);$$

a relation whose theoretical bearings will be discussed in the following chapter.

SUMMARY OF RESULTS AS TO THE INFLUENCE OF THE LIGHT ON PHOTO-ELECTRIC EMISSION

Intensity.

For a given source

- (1) the number of electrons emitted per unit time is directly proportional to the intensity ;
- (2) the velocity of the electrons is independent of the intensity.

Plane of Polarisation.

In the case of the *normal* effect

- (1) the number of electrons liberated is only affected by the orientation of the plane of polarisation in so far as the absorption of light depends upon it (Pohl) ;
- (2) the maximum velocity of emission is independent of the orientation of the plane of polarisation (Pohl).

In the case of the *selective* effect

- (1) the number of electrons liberated is much greater when the electric vector vibrates in the plane of incidence (Elster and Geitel, Pohl and Pringsheim) ;
- (2) the same result as for the normal effect (Elster and Geitel).

Frequency.

For a given intensity in the case of the *normal* effect

- (1) the number of electrons emitted per unit time increases with the frequency of the light (Ladenburg, Mohlin, Hallwachs) but probably reaches a maximum in the extreme ultra-violet (Compton and Richardson) ;
- (2) the velocity of the electrons increases with the frequency of the light. (Kinetic energy a linear function of the frequency.)

In the case of the *selective* effect the number of electrons emitted has a maximum value for a particular frequency.

CHAPTER XI

THEORIES OF PHOTO-ELECTRIC ACTION

Two important questions require consideration in connection with the theory of photo-electric action. Assuming that the essential feature of such action is the liberation of electrons by light, we must ask : (1) How can we classify the electrons which are set free under the influence of light ? (2) How do these electrons obtain the energy required for their emission from the surface with the observed velocities ? These questions, which are to some extent interdependent, can scarcely be answered definitely at the present time. In this chapter we shall summarise the principal answers that have been given, and point out some of the difficulties that require investigation before a satisfactory theory of photo-electric action can be regarded as established. The chapter may be looked upon as containing an outline of the theories suggested for the solution of the problem rather than a complete and final discussion.

We may classify the electrons associated with matter somewhat as follows :

1. The so-called " free " electrons, to which the electrical conductivity of a metal is due. According to one view these can wander freely between the atoms with velocities in agreement with the laws of the kinetic theory of gases. According to another they are handed on from one atom to another, in such a way that, in the presence of an electric field, a continuous transference of electrons takes place through the material.

2. The " dispersional " or " emission " electrons, which give rise to the absorption of light by the substance and at higher temperatures give out radiation. These electrons are responsible for the phenomena of the Zeeman effect.

3. The "valency" electrons (eight as a maximum), which correspond to the chemical "bonds" or "valencies," and cause through their passage to another atom the electropositive valency of the atom they have left.

4. The "photo-electric" electrons, which are separated from the atom under the influence of light.

It is probable that some of these classes are really identical; for instance, the dispersional electrons have been regarded as identical with the valency electrons. On the other hand, J. J. Thomson* suggests that when an atom of an element is giving out its spectrum, it is surrounded by a swarm of corpuscles. The characteristic spectrum lines may then be due to the vibrations of systems or groups of corpuscles, which are not permanent but yet last sufficiently long for the emission of a large number of vibrations. Thus the lines of the spectrum would be due to the vibrations, not of the corpuscles inside the atom, but of the corpuscles in the field of force outside the atom.†

We have to consider whether we can identify the last class—the photo-electric electrons—with any one of the three preceding. In attempting such an identification we must bear in mind that the electrons concerned in the "selective" photo-electric effect may not belong to the same class as those which give rise to the "normal" effect.

The work of Pohl and Pringsheim certainly suggests that the electrons of the selective effect are connected with the chemical binding of the atom—that is, with the valency electrons. According to the theory of Stark‡ also, the electrons of the photo-electric effect are the valency electrons. When a metal enters into combination more energy is required to separate the valency electron than before. This means that

* J. J. Thomson, *Phil. Mag.*, 11, p. 774, 1906.

† The phraseology here used implies the possibility of distinguishing between the "inside" and the "outside" of an atom, as in the case of the atomic model suggested by J. J. Thomson in which a sphere of positive electricity containing a certain number of corpuscles is postulated. Such a distinction can hardly be maintained if we adopt the Saturnian model suggested by Rutherford in which a small positive nucleus is supposed to be surrounded by rings of corpuscles.

‡ Stark, *Phys. Zeit.*, 10, p. 787, 1909.

light of shorter wave-length is then needed to effect the separation.

Lenard distinguishes between the photo-electric electrons and the emission electrons, and on this distinction bases his theory of phosphorescence. The excitation of a phosphorescent substance by light consists in the separation of the photo-electrons. These on their return to the atom set in vibration the emission electrons, so giving rise to the luminescence.

Again, it might be suggested that the electrons concerned in the "normal" photo-electric emission from a metal are identical with those of the first class. If we adopt the prevailing view that metallic conduction is due to the presence of "free" electrons, which can wander between the atoms with velocities in accord with those given by the laws of the kinetic theory of gases, we might suppose that the velocity of certain of these electrons is so augmented by the electric vector in the light wave as to be able to leave the surface. Against this view we have the fact that the photo-electric current in a good vacuum is independent of the temperature. A further argument against it is afforded by the experimental result that the initial velocity is, over a very wide range, independent of the intensity of the light. This difficulty can, however, be overcome by a special hypothesis as to the nature of light, which will be considered later in the chapter.

We conclude that the electrons concerned in the photo-electric effect are probably derived from the number more or less closely bound up with the atom, the natural view to take being that those electrons which are less firmly bound to the atom would, under suitable conditions, be the first to leave the system.

The second question to be considered is that of determining the way in which electrons can acquire sufficient energy to escape from a metal surface under the influence of light. There appear to be three possible theories as to the method by which the energy of the electron can be sufficiently increased by the communication of energy from a train of light waves,

In the first place, we can imagine that atoms or complex atomic systems become unstable under the influence of light, and project electrons from themselves by a process which might be described as an explosion. In this case the velocity of projection would be approximately that possessed by the electron within the atom.

Secondly, we may suppose that, as the electric vector in a Röntgen pulse can detach an electron from the atom, so the electric vector in a half wave-length of light can also, in favourable circumstances, detach an electron whose energy would be derived directly from that of the light.

Thirdly, we may suppose that the electrons, which must be regarded as having certain free periods of vibration, are set in resonant vibration by light-waves whose period agrees with their own, and so acquire sufficient kinetic energy to break away from the atom.

1. The first view put forward is that the electron is expelled by a process that might be described as an explosion resulting from the instability of the atomic system or systems induced by light. This is obviously suggested by the prevailing theory of radio-activity, and is equivalent to saying that in the photo-electric effect we have a kind of induced radio-activity. In this case the energy of the escaping electrons would be derived from the internal energy of the atomic systems.

The hypothesis presents attractive possibilities, but cannot, I think, be seriously upheld at the present time. Radio-active processes, so far as our knowledge goes, are entirely independent of external conditions. Photo-electric activity is not an atomic property. The initial velocity of the photo-electric corpuscles varies in a continuous way with the frequency of the light; such a result would require special assumptions to explain it were the energy the result of an explosion of the atoms.

2. According to the second view the electron (whether "bound" or "free") is liberated in consequence of the velocity imparted to it by the passage of a half-wave of light. The kinetic energy of the emitted electron is derived directly from the energy of the incident light.

This view presents serious difficulties. In the first place the magnitude of the initial velocity (of the order 8×10^7 cm. per sec. for aluminium, corresponding to a fall of the electron through a potential difference of 3 volts) is too large for it to come from a half-light-vibration of usual intensity, for, according to the ordinary electro-magnetic theory, potential differences of 3 volts are not met with in such light. In the second place, the velocity of emission does not depend on the intensity of the light when using a given source.

Sir J. J. Thomson has put forward a theory as to the nature of light which helps to meet these difficulties. It is similar in character to the "quantum theory" developed by Planck and Einstein, which supposes that the energy in radiation is concentrated in discrete units. Although these theories are in accord with many of the facts of photo-electricity, they are not accepted at the present time without considerable reserve, mainly because they cannot be reconciled with the fundamental electro-dynamic equations of Maxwell and Hertz.

J. J. Thomson* supposes that the ether through which the light is travelling has disseminated through it discrete lines of electric force. The energy travelling outwards with the wave is not spread uniformly over the wave front, but is concentrated over those parts of the front where the pulses are travelling along the lines of force. Thus the front of a Röntgen pulse or a wave of light would suggest the appearance of a number of bright spots on a dark ground. "From this point of view the distribution of energy is very like that contemplated on the old emission theory, according to which the energy was located on moving particles sparsely disseminated throughout space. The energy is, as it were, done up into bundles, and the energy in any particular bundle does not change as the bundle travels along the line of force." On the basis of this hypothesis it is possible to explain the remarkably small ionisation produced in a gas by Röntgen radiation or ultra-violet light; when the ionisation is strong, the ratio of the free ions to the number of gas molecules is less than $1 : 10^{12}$. This view of the structure of light renders

* J. J. Thomson, *Proc. Camb. Phil. Soc.*, **14**, pp. 417-424, 1906-8.

plausible the proportionality between the number of electrons emitted and the intensity of the light, and the independence of the velocity of emission on that intensity. "Thus, if we consider light falling on a metal plate, if we increase the distance of the source of light we shall diminish the number of these different bundles or units falling on a given area of the metal, but we shall not diminish the energy in the individual units. Thus any effect which can be produced by a unit by itself will, when the source of light is removed to a greater distance, take place less frequently, it is true, but when it does take place it will be of the same character as when the intensity of the light was stronger."

The quantum or unitary theory of light (Lichtquanten-hypothese) is derived from the work of Planck * on the radiation laws of a black body. The energy of radiation is supposed to be built up of an integral number of finite elements. Planck finds that such a quantum of energy ϵ has the value

$$\epsilon = h\nu,$$

where ν is the frequency of vibration, and $h = 6.55 \times 10^{-27}$ erg. sec.

Einstein † extended the hypothesis, and showed that monochromatic radiation of small density, obeying Wien's radiation law, behaves as though it consisted of energy or light units of magnitude $h\nu$. He makes the hypothesis as to the nature of light general, and assumes that when light diverges from a point, the energy is not continuously divided over a space that ever grows larger and larger, but that it is composed of a finite number of quantities of energy. These units of energy move outwards without dividing, and can only be absorbed or emitted as wholes. By means of this hypothesis Einstein sought to explain such phenomena as the photo-electric effect, the ionisation of gases by ultra-violet light, photo-luminescence, and the theory of specific heat.

According to the unitary theory of light the photo-electric emission of an electron is to be explained by supposing that

* Planck, *Ann. d. Physik*, **4**, p. 553, 1901.

† Einstein, *Ann. d. Physik*, **17**, p. 132, 1905.

the kinetic energy of the electron is augmented by energy derived from one light unit. Hence arises the proportionality between the number of electrons emitted and the intensity of radiation, and also the independence of the energy (or velocity) of the electron on the energy or intensity of the active light, although the electron's energy is, in part at least, derived from the energy of the light.

When the light unit gives up its energy, only a definite fraction of that energy may be transferred to the electron, but the simplest assumption to make is that the whole energy is given to a single electron. In this case the electron leaves the body with energy

$$\frac{1}{2}mv^2 = h\nu - P;$$

where P is the work the electron has to do in leaving the body. If V denote (in E.S.U.) the positive potential which is just sufficient to prevent the discharge of electricity from the body,

$$Ve = \frac{1}{2}mv^2 = h\nu - P.$$

3. The third view attributes the expulsion of electrons to resonance. The electrons are set in resonant vibration by the incident light, and acquire sufficient velocity to enable them to escape from the atom.

Some of the difficulties met with in regard to the second view are encountered again here. Imagine an electron executing linear vibrations about a position of equilibrium, and suppose that when the amplitude of the vibration exceeds a certain definite limit the electron passes beyond the range of the attractive forces binding it to the atom. If light of the same period is incident upon it, so as to excite linear resonance vibrations, the amplitude of the vibrations will go on increasing. When the amplitude reaches the limit assigned above, the electron would be free from the atom, but its velocity would be zero. To enable it to leave the atom with finite velocity it must acquire an overplus of kinetic energy, and this overplus must have been acquired during the last half of the whole resonance vibration. Thus we see that the initial velocity with which the electron escapes from the atom is derived directly from the light, and

as in the second view, from one half-vibration. We should then expect the initial velocity to increase with the intensity of the light.

To avoid the difficulties here met with Lenard assumes the existence of complicated conditions of motion of the electron within the body, and that the initial velocity is not derived from the light energy, but from the energy of those movements already existing before illumination takes place. In this case the resonance vibrations only play a liberating rôle.

Thus imagine an electron describing a circular orbit in the interior of an atom. If light falls upon it with an electric vector parallel to the line AB, the orbit will be disturbed, and we can suppose that the amplitude of the resonance vibrations parallel to AB increases till the electron reaches a point such as A (the extremity of the major axis of an elliptic orbit), where it is outside the range of attraction of the atom. The electron would then travel off at a tangent with a velocity equal to that with which it was moving in its orbit. The initial velocity would thus be independent of the intensity of the active light. On the other hand, we can see that there would be a relation between the initial velocity and the frequency of the light.

Such a relation has been investigated by Lindemann * and applied to the "selective" photo-electric effect when the vibrations of the electric vector are in the plane of incidence. He assumes that an electron is describing an elliptic orbit about a positive nucleus, and that the distance of the electron from the centre of the atom is one-half the distance between the atoms. Then as in Kepler's treatment of a planetary orbit the time of revolution is $2\pi r^3/(ne^2/m)^{\frac{1}{2}}$, where r is the distance apart, n is the valency, and e and m the charge and the mass of the electron. If the incident light has the same period, the eccentricity of the ellipse becomes greater and greater till the motion becomes unstable and the electron leaves the atom.

In order to connect r with known magnitudes a tetrahedral

* Lindemann, *Verh. Deutsch. Phys. Gesell.*, 13, pp. 482-488, 1911.

arrangement of atoms is assumed, and r is then found to be $2\frac{1}{2} \times (A/Nd)^{1/2}$, where A is the atomic weight, d the density, and $N=6 \times 10^{23}$. The value of r calculated for potassium is 2.37×10^{-8} , and the corresponding wave-length for maximum resonance is $\lambda=438 \mu\mu$.

For other metals the wave-length can be calculated from the formula $\lambda=65.3 \sqrt{(a/n)}$, where a is the atomic volume. The values so calculated are in good agreement with those determined experimentally by Pohl and Pringsheim * (p. 128).

	Li	Na	K	Rb	Cs	Ca	Sn	Ba	Mg
λ (calculated)	225	317	438	490	550	233	271	280	172
λ (observed)	280	340	435	480	280	...

The calculated value of the wave-length giving the maximum selective effect for calcium lies within the range of wave-lengths used by Hughes in the experiments previously described (p. 136). Yet nothing abnormal was found with regard to the emission velocities from freshly-distilled calcium as compared with the other metals investigated. Pohl and Pringsheim † found no selective effect with a freshly-distilled surface of magnesium, but such an effect showed itself distinctly in less than one hour after distillation, the maximum being at $250 \mu\mu$. Magnesium was one of the metals investigated by Hughes, who found nothing peculiar in the emission velocities. He concludes that the emission velocities appear to be unaffected by the presence of a selective effect.

The results already quoted justify us in accepting the selective emission of electrons as a resonance phenomenon, and the balance of probabilities appears to be in favour of regarding the normal photo-electric effect also as being due to resonance.

J. J. THOMSON'S THEORY OF RADIATION

A theory of radiation has been suggested by J. J. Thomson, ‡ in which the radiation is regarded as arising from the

* Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Gesell.*, **14**, pp. 46-59, 1912.

† *Ibid.*, p. 546, 1912.

‡ J. J. Thomson, *Phil. Mag.*, **14**, pp. 215-231, 1907; **20**, pp. 238-247, 544, 1910.

impact between electrons and the molecules of the body. In order to conform with the Second Law of Thermodynamics it is supposed that the forces exerted during the collision between a corpuscle and a molecule vary inversely as the cube of the distance between them, and further, that the collision may be regarded as taking place, not between the corpuscle and the molecule as a whole, but between the corpuscle and a system such as an electric-doublet of constant moment with its negative end pointing to the corpuscle. Such doublets may be supposed dispersed through the molecules, the systems being of the same character in whatever molecules they are found. If AB is a doublet with the positive end at B, a corpuscle P can have a state of steady motion when P describes a circle whose plane is perpendicular to AB and whose centre lies on AB produced. This steady motion is not permanent, for if the particle were started with a radial velocity it would slowly drift away. But we may suppose the system to remain in this state during the time occupied by a few light vibrations.

It is shown that in such motion the kinetic energy is proportional to the frequency. If a light wave of the same frequency passes through the body, the electric forces in the wave might tend to twist the axis of the doublet so as to alter the angle between that axis and the direction of the corpuscle, and if the alteration produced by resonance is sufficiently great the corpuscle might be liberated with practically the same kinetic energy as it possessed in the steady motion. Thus the energy of emission would be proportional to the frequency of the light. Since systems having the proper frequency may occur only in a small number of molecules, we can explain why the number of particles emitted is found to be small compared with the total number of molecules passed over.

In discussing at a later date* the "unit theory" of light J. J. Thomson points out that in all cases where this conception of the unitary character of light is helpful we have to deal with transformation of energy. He suggests that when-

* J. J. Thomson, *Proc. Camb. Phil. Soc.*, **16**, pp. 643-652, 1912.

ever there is a transformation of radiant energy into thermal energy or thermal energy into radiant energy, there is an element of discontinuity in the process, inasmuch as it takes place by jumps. Thus, to illustrate the absorption of monochromatic light, let us imagine that we have a frictionless perfectly elastic spring supporting a charged body. If this were acted on by electric waves of its own period it would absorb energy from the waves. But after the waves had passed over it the spring would go on vibrating for some time, and would radiate away its energy in the form of electric waves of the same period as the primary waves incident upon the spring—that is, we should have merely a scattering of the primary wave and not real absorption. In order to get real absorption we may imagine that the spring snaps when the charged body has acquired a certain amount of energy, then the spring would act as a true absorber of energy, for the periodic character of the original energy would have disappeared. With a system of springs of this kind the energy absorbed would always be a multiple of a definite unit, namely, the energy required to break the spring.

Suppose, in the next place, that we think of a system containing molecules and corpuscles upon which monochromatic radiation is incident. Interchanges of energy will take place between the various constituents of the system. The properties of gases indicate that there is no approach to anything like equipartition of energy between the corpuscles and the atoms and molecules. In such a case there is a possibility that the corpuscles should get into equilibrium with the radiation rather than with the molecules. Those corpuscles which are in resonance with the monochromatic light would dissipate their energy as light-waves, and the light would be scattered but not absorbed. But if the corpuscle received that amount of energy which is sufficient to detach it from the system, so much energy would disappear from the radiation, and absorption would take place. In this way we can understand how absorption of energy can take place in a discontinuous manner. If we suppose that the return of an unattached corpuscle to its system is the cause of radiation,

the amount of energy radiated will likewise be finite and definite.

The supposition that the energy of the corpuscles might differ from that required for equilibrium with the molecules according to the kinetic theory would account for the want of dependence of the photo-electric emission on temperature.

RICHARDSON'S THEORY OF PHOTO-ELECTRIC EMISSION

O. W. Richardson * has discussed the emission of electrons from a body exposed to radiation on the view that metals contain a large number (n per c.c.) of free electrons, which are retained within the metal by the action of forces near the boundary, giving rise to work functions w_1 , w_2 , &c., characteristic of each metal. These electrons are dynamically equivalent to the molecules of a gas. The work done in taking an electron from a point A to a point B is

$$W = R\theta \log \frac{n_1}{n_2},$$

where R is the gas constant calculated for a single molecule, θ is the absolute temperature, and n_1 , n_2 , are the concentrations of the free electrons at A and B respectively. From this it follows that at any point in an insulated enclosure

$$R\theta \log n + \omega = C,$$

where ω is the time average of the potential energy of an electron and C is constant at every point inside the enclosure, but may be a function of temperature. It is shown, on the basis of thermodynamic and statistical principles, that the number N of electrons emitted from unit area of a body in equilibrium with the complete radiation characteristic of its temperature θ , may be expressed in either of the two equivalent forms

$$N = \frac{c}{4} \int_0^\infty \epsilon F(\nu_1 \theta) E(\nu_1 \theta) d\nu,$$

and

$$N = \alpha A \theta^2 e^{\int \frac{w}{R\theta^2} d\theta};$$

* O. W. Richardson, *Phil. Mag.*, **23**, p. 615, 1912; **24**, p. 570, 1912.

where $E(\nu, \theta)$ is the function which expresses the distribution in the spectrum of the steady energy density, $eF(\nu, \theta)$ is the number of electrons emitted in the presence of unit energy whose frequency lies between ν and $\nu + d\nu$, c is the velocity of light, A is a constant characteristic of the substance and independent of θ , α is the proportion of the returning electrons which are absorbed, w is the internal latent heat of evaporation for one electron, and R is the gas constant for one molecule.

Assuming, as a convenient approximation, that

$$w = w_0 + \frac{3}{2} R\theta,$$

where w_0 is independent of θ , and that $\alpha = 1$ —i.e. that there is no reflection of the incident electrons, the second equation reduces to

$$N = A\theta^2 e^{-\frac{w}{k\theta}}.$$

If, instead of using Planck's formula for $E(\nu, \theta)$, we replace it by the approximation (Wien's form),

$$E(\nu, \theta) \approx \frac{8\pi}{c^3} h\nu^3 e^{-\frac{h\nu}{k\theta}}$$

we obtain an integral equation for $eF(\nu)$ which is satisfied by the values

$$eF(\nu) = 0, \quad \text{when } 0 < h\nu < w_0;$$

$$\text{and by } eF(\nu) = \frac{A_1 h}{R^2 \nu^2} \left(1 - \frac{w_0}{h\nu} \right), \quad \text{when } w_0 < h\nu < \infty;$$

$$\text{where } A_1 = c^2 A / 2\pi.$$

These expressions for the number of electrons emitted under the influence of light of a particular wave-length show that there is a limiting value

$$\nu_0 = \frac{w_0}{h}$$

below which no photo-electric emission takes place.

It is shown further that the average kinetic energy T_r of the electrons which are emitted by light of frequency ν is given by

$$T_r = h\nu - w_0, \quad \text{when } w_0 < h\nu < \infty.$$

This assumes that reflection of electrons can be neglected. If this is not the case we can put

$$T_r = s(h\nu - w_0), \text{ when } w_0 < h\nu < \infty,$$

where s is a positive quantity less than unity. By putting $s=1$ we obtain the maximum kinetic energy for the given frequency.

"The above equations have been derived without making use of the hypothesis that free radiant energy exists in the form of 'light quanta,' unless this hypothesis implicitly underlies the assumption (A) that Planck's radiation formula is true, (B) that the number of electrons is proportional to the intensity of monochromatic radiation. Planck has recently shown that the unitary view is not necessary to account for (A), and it has not yet been shown to be necessary to account for (B)." Hence the confirmation of the equations does not necessarily involve the acceptance of the unitary theory of light.

The maximum and the mean energies of the electrons emitted under the influence of light can be determined from the velocity distribution curves. Richardson and Compton find that the experimental results can be represented fairly accurately by writing

$$\text{Maximum energy} = T_m = k_m(\nu - \nu_0);$$

$$\text{Mean energy} = T_r = k_r(\nu - \nu_0).$$

The following table gives the numerical values of the constants:

Metal.	Values from T_m .			Values from T_r .		
	$\nu_0 \times 10^{-13}$	λ_0 .	k_m .	$\nu_0 \times 10^{-13}$	λ_0 .	k_r .
Na .	51.5	583	5.2	52	577	2.6
Al .	63	477	4.3	73	411	2.6
Mg .	78.5	382	5.2	80	375	2.55
Zn .	80	376	5.1	84	357	2.8
Sn .	83	362	4.9	89	337	2.75
Bi .	91	330	3.55	89	337	1.9
Cu .	100	300	3.8	97	309	1.65
Pt .	104	288	5.85	103	291	2.8

The unit for λ_0 is $1 \mu\mu$, and for k_m and k_r is 10^{-27} erg. sec. The values of ν_0 or λ_0 obtained from the maximum energy agree with those obtained from the mean energy except in the case of aluminium. The authors attach more weight to the values from the mean energy.

The values of k_m are fairly concordant except in the case of copper and bismuth, and are about 20 per cent. less than the theoretical value corresponding with the formula

$$T_m = h(\nu - \nu_0),$$

where h is Planck's constant, 6.55×10^{-27} erg. sec. The values of k_r are approximately one-half the corresponding values of k_m , including copper and bismuth—that is, the value of s in the formula

$$T_r = s h(\nu - \nu_0)$$

is very close to one-half.

A further test of the theoretical formula is afforded by a consideration of the term $w_0 = h\nu_0$. The latent heat of evaporation of electrons at the absolute zero of temperature can be calculated from measurements of the saturation electronic current at different temperatures. The mean value of w_0 so obtained is 5.34 volts, or 8.32×10^{-12} erg, in the case of platinum. The value of ν_0 is 1.04×10^{15} sec.⁻¹, whence $h = w_0/\nu_0 = 8.07 \times 10^{-27}$ erg. sec. This value of h is fairly close to the radiation value.

The theory led to an expression connecting the values of w_0 for two metals, from which it appears that the difference between the two values of w_0 is approximately equal to the contact difference of potential between the metals in question.

The experimental results obtained by Richardson and Compton may be compared with those already recorded for distilled metal surfaces by Hughes (p. 137), who used a formula for the initial velocities of the same type as that deduced by Richardson. To facilitate the comparison, the following table has been prepared giving the values for the maximum energy in the case of the metals magnesium, zinc, and bismuth, common to both sets of experiments.

Metal.	Richardson and Compton.		Hughes.	
	λ_0 .	h_m .	λ_0 .	h_m .
Mg . . .	382	5.2	33°	5.32
Zn . . .	376	5.1	302	5.95
Bi . . .	330	3.55	323	5.70

In each case the initial velocity as measured by Hughes is greater than the corresponding velocity for the surface obtained by scraping the metal. The wave-length at which the emission of electrons sets in is less in the experiments of Hughes than in the results recorded by Richardson and Compton. Greater weight must be given to the observations secured with surfaces produced by distillation in a high vacuum.

It has been pointed out by Hughes* that in all these experiments the maximum velocities investigated are those of electrons emitted from the side of the plate on which the light was incident. Now, from the results of Robinson (p. 46) for platinum, it may be inferred that originally all the electrons are, perhaps, emitted more or less in the direction in which the light is travelling, and that the energy lost by a photo-electron in swinging round from its original direction of emission is at least 11 per cent. The difference appears to be sufficient to account for the value of h_m for platinum being less than Planck's constant h . In other words, the results of the quantum theory and of Einstein's formula may be applied in the case of platinum, and presumably in other cases also, if we keep in mind the electrons which emerge in the direction of the incident light. If this be borne out by further experiment, we reach the important conclusion that for light of given frequency, electrons acquire the same energy in the case of all metals, though the work done in escaping, w_0 , is a quantity characteristic of the metal.

The question of the *number* of electrons emitted in unit

* Hughes, *Phil. Mag.*, 25, pp. 683-686, 1913.

time has been discussed by Compton and Richardson * in a paper recently published. It is shown that the suggested solution of the integral equation is capable of predicting accurately the values of the wave-length corresponding to no emission and to maximum emission respectively, but the experimental results point to the existence of another term in the solution. For the curve showing the relation between the number of electrons emitted and the wave-length appears to possess two maxima instead of only a single maximum. One term may be required to account for the "selective," and another for the "normal" photo-electric effect. Such a solution of the theoretical equations has not, as yet, been discovered.

* Compton and Richardson, *Phil. Mag.*, **26**, pp. 549-567, 1913.

CHAPTER XII

PHOTO-ELECTRIC FATIGUE

THE fact that the photo-electric activity of a metal surface which has been freshly polished diminishes with the time has been known almost as long as the existence of the photo-electric current. In the experiments of Hertz it was noticed that the illuminated metal terminals between which the spark was to pass required careful polishing; tarnished terminals showed no increase in the spark-length when illuminated by ultra-violet light.

Many of the earlier experimenters noticed that the photo-electric current from metals such as zinc or aluminium diminished as the time that had elapsed since the metal was polished was increased. Hallwachs also found a diminution in the positive potential reached by a metal plate when illuminated, after the plate had been used for some time. This diminution in photo-electric activity is known as the "fatigue" of the Hallwachs effect.

In his first paper on photo-electric phenomena Hallwachs * remarked that the "ageing" of the surface is accelerated by the influence of the illumination. Again,† in describing the experiments showing that a metal becomes positively electrified under the influence of light, he states that "old surfaces no longer show the phenomenon. The radiation itself lowers the potential to which the plates can be electrified, so that with any succeeding experiment made with the same surface the potential obtained is lower, while the rise to it takes place more rapidly, and the decrease is greater than when for the same interval of time between the experiments the plate was not illuminated." In a later paper ‡ he pointed out that this

* Hallwachs, *Wied. Ann. d. Physik*, **33**, p. 308, 1888.

† Hallwachs, *Phil. Mag.* (5), **26**, p. 78, 1888.

‡ Hallwachs, *Ann. d. Physik*, **37**, pp. 666-675, 1889.

change was not due to oxidation of the surface, at least in the case of a copper plate. The activity of an oxidised plate was the same as that of a polished plate. The presence of water vapour was without effect. A copper plate oxidised by heating in air can be used as a standard, as the activity assumes a constant value which changes but little with the time.

Photo-electric fatigue was noticed by Hoor.* When a freshly-polished plate of zinc was illuminated by an arc lamp for 20 seconds a diminution of 35.4 per cent. took place in a negative charge communicated to an electroscope in connection with it. With copper the diminution was 37 per cent., with brass 38 per cent. After the plates were exposed for 48 hours in the open air the diminution in the charge was about the same for all three metals—viz. 10 per cent.

Stoletow † notes that when two condensers are used at the same time, one being nearer the source of light than the other, that which is nearer the source fatigues more rapidly than the other, so that the ratio of their sensibility varies when the exposure is prolonged.

Elster and Geitel ‡ found that a freshly-polished surface of zinc lost half its photo-electric sensitiveness in five minutes, sunlight being used in making the test.

Branly,§ again, drew attention to the fact that metal surfaces were extremely active when freshly polished, sunlight being then sufficient to produce the discharge. An aluminium disk tested about 35 minutes after polishing showed about one-third of the initial activity.

THEORIES OF PHOTO-ELECTRIC FATIGUE

Various theories as to the nature of the change producing photo-electric fatigue have been advanced. These may be summarised as follows :

1. A chemical change, such as oxidation of the surface. (Knoblauch.)

* Hoor, *Akad. Wiss. Wien. Ber.*, **97**, p. 723, 1888.

† Stoletow, *C. R.*, **108**, pp. 1241–1243, 1889.

‡ Elster and Geitel, *Wied. Ann. d. Physik*, **38**, p. 503, 1889.

§ Branly, *Journ. de Physique* (3), **2**, p. 300, 1893.

2. A physical change of the metal itself, as, for example, a roughening of the surface.
3. An electrical change in the formation of an electrical double layer. (Lenard.)
4. A disintegration of the metal due to the expulsion of electrons by light. (Ramsay and Spencer.)
5. A change in the surface film of gas, or in the gas occluded in the metal. (Hallwachs.)

It must be kept in mind that the cause of such a phenomenon as photo-electric fatigue is not necessarily the same in all cases. What may be a primary cause of fatigue in one case may play only an unimportant part in other cases. Thus oxidation would bring about a rapid diminution in the activity of an alkali metal exposed to air, but it does not follow that the fatigue of other metals is in all cases due to the same cause. As many confusing and contradictory results have been obtained by different experimenters, it is most important to pay attention to the exact conditions under which fatigue takes place in any particular instance. In dealing with this subject it is convenient to distinguish between the rapid fatigue that takes place when a plate, say of copper or zinc, is exposed in a gas at ordinary pressures, and the slow fatigue sometimes observed in a vacuum.

PHOTO-ELECTRIC FATIGUE IN GASES AT ORDINARY PRESSURES

In discussing this case we may ask four questions, which can only be answered by experimental investigation. Firstly, is light the active agent in producing fatigue? Secondly, does fatigue depend on the size of the containing vessel? Thirdly, does fatigue take place in gases other than air? Fourthly, does fatigue depend on the electrical condition of the plate? On the answers obtained depends the choice of the correct theory of the main cause of fatigue.

1. *Is Light the Active Agent in producing Fatigue?*—We have seen that in the early literature of the subject fatigue was often attributed to the direct action of the light.

Kreusler,* who was the first to investigate fatigue effects systematically, expressly states that the fatigue depends on an action of the ultra-violet light on the surface of the kathode. This is shown by the following experiment. The photo-electric current with a potential of 3,320 volts was measured several times in succession, using a kathode of freshly-polished zinc. Between two measurements the kathode remained in connection with the earth—that is, at zero potential. During this interval it was either illuminated for several minutes or shielded from the light (a 2 mm. spark between Al terminals). The following table illustrates the results :

Intensity of Photo-electric Current.	
	Amp.
Initial	1.36×10^{-10}
After 8 minutes in darkness	1.33×10^{-10}
After 5 minutes in light	1.16×10^{-10}
After 6 minutes in darkness	1.16×10^{-10}
After 5 minutes in light	1.02×10^{-10}
After 5 minutes in darkness	1.02×10^{-10}
After 6 minutes in light	0.85×10^{-10}

The fatigue is proportional to the duration of the illumination.

It should be noticed that in these experiments very large potential differences were employed.

About the same time Buisson † carried out a series of experiments which led him to the conclusion that a modification of a metallic surface was brought about under the influence of light. The properties investigated were the photo-electric activity and the contact difference of potential.

“Immediately after cleaning, the speed of (photo-electric) discharge is extremely great, but it lessens regularly towards zero. The rapidity, but not the mode of this diminution, depends on the richness of the light in ultra-violet rays.

“This variation of sensitiveness is not essentially due to an alteration, such as oxidation, produced by the air alone. It is light which is the active agent. In fact, such a plate

* Kreusler, *Ann. d. Physik*, **6**, p. 398, 1901.

† Buisson, *Annal. Chim. Phys.*, **24**, pp. 320–398, 1901.

left several hours in darkness after having been cleaned, and then exposed to light, behaves like a fresh plate, and further, its sensitiveness is considerably increased. Lastly, the diminution of sensitiveness which light produces on the metallic surface is not permanent. It disappears in darkness, and after a stay of sufficient duration away from the light, the plate behaves as if it had never been exposed.

"The results are clearest with amalgamated zinc, with which one can obtain a perfectly new surface by strongly wiping the metal. With zinc and aluminium it would appear that, in addition, the action of light produces a slow permanent alteration, such as oxidation."

The variation of the photo-electric sensibility was also attributed to the action of light by E. v. Schweidler.* The substances tested were zinc, magnesium, amalgamated zinc and magnalium, and the fatigue was found to be due chiefly to "effective," *i.e.* ultra-violet, light. The process of recovery, which is not dependent on the light, may be superposed on the process of fatigue, so that the two go on simultaneously.

The interpretation put upon the recorded results was first called in question by Hallwachs,† who came to the conclusion that under ordinary conditions light is not a primary cause of photo-electric fatigue. He pointed out that, owing to the size of the containing vessel influencing the rate at which fatigue takes place, experiments in light and in darkness were not comparable unless the size of the vessel were unchanged. Experiments carried out with two zinc plates in sunlight and in complete darkness showed no difference in the rate of fatigue.

		Percentage Fatigue.		
In light	40	78	88	93
In darkness	44	81	88	94
Time in minutes	6	24	52	135

The use of photo-electric cells with plates of Cu or CuO for the photometry of ultra-violet light was only possible in

* E. v. Schweidler, *Akad. Wiss. Wien. Ber.*, **112**, IIa, p. 974, 1903.

† Hallwachs, *Phys. Zeit.*, **5**, p. 489, 1904.

view of the fact that prolonged exposure to the radiation had no influence on the activity. In the course of his researches Hallwachs never found a recovery of activity that could be attributed to the plate being kept in *darkness*. Though the radiation is not the direct cause of fatigue, it may in certain cases be a secondary cause, as through the production of ozone, which is found to bring about a diminution of the photo-electric activity.

F. Aigner * disputed the conclusions of Hallwachs, and described experiments from which he inferred that changes in photo-electric activity are due directly to the illumination; the shorter the wave-length, the more active is the light, as a rule, in producing fatigue.

E. Ullmann † has repeated the experiments of Aigner with a view to discovering why his results showed evidence of an influence of light on the fatigue of zinc. Two zinc plates in two similar testing vessels were tested at the beginning and at the end of a period of five minutes, during which one was in darkness while the other was illuminated by an arc lamp. With the lamp distant 120 cm. from the plates no difference could be detected in the percentage fatigue. The same was true with the lamp 46 cm. from the plates; but when the distance was reduced to 23 cm. the illuminated plate was found to fatigue more rapidly than the plate in darkness. The difference was attributed in part to the formation of ozone by the ultra-violet light, in part to the action of heat on the plate. To discriminate between the effects, the fatigue was measured when the illumination was (a) direct, (b) tangential, (c) on the back of the plate. The conclusion drawn from these experiments was that illumination produced no direct fatigue, but that the fatigue observed by Aigner must be attributed to the influence of ozone, diminished by the influence of the increased temperature.

The results obtained by H. S. Allen ‡ in his earlier papers

* F. Aigner, *Akad. Wiss. Wien, Sitz. Ber.*, **115**, 2a, pp. 1485-1504, 1906.

† E. Ullmann, *Ann. d. Physik* (4), **32**, pp. 15-20, 1910.

‡ H. S. Allen, *Proc. Roy. Soc., A*, **78**, § 7, p. 489, 1907; **82**, § 5, p. 164, 1909.

on the photo-electric fatigue of polished and amalgamated zinc are in agreement with the view of Hallwachs. He found that the rate at which the fatigue proceeded was not greatly influenced by the intensity or character of the source of light employed. In his later work * he has shown that the fatigue takes place in complete darkness almost as rapidly as in light. Thus we conclude that light is not the primary cause of fatigue, though it may play a secondary part in accelerating or retarding fatigue.

The effect of light of longer wave-length in increasing the activity—an effect mentioned by several experimenters—is almost certainly due to a rise in temperature. This is illustrated in Fig. 34, p. 170, where the upper curve shows an apparent recovery of the plate due to the thermal radiation, while the lower curve shows the normal fatigue that occurs when the longer waves are absorbed by a layer of water.

2. Does Fatigue depend on the Size of the Containing Vessel?—

The influence of the size of the containing vessel (Gefäßeinfluss) on the rate at which fatigue proceeds was first noticed by Hallwachs.† Highly-polished copper plates were placed in a photo-electric cell immediately after polishing, and their photo-electric activity determined. They were then removed from the cell and placed in various receptacles, from which they were taken from time to time for measurements of their activity to be made in the cell. Plates lying in the open air showed a fall to half the original activity in about 1.5 hours, while those in the room required twice as long for the same fall to take place. If the plates were put in a large glass vessel of 0.5 cubic metre capacity, the activity fell to half-value in 22 hours, and if the plates were put in a 1-litre flask, no less a period than from 8 to 20 days was necessary.

A plate of copper oxide (CuO) is much more constant. In a room the activity falls to half-value in about 13 days—about 100 times the period for the copper plate. With the CuO

* H. S. Allen, *Ann. d. Physik*, **32**, p. 1111, 1910; *Phil. Mag.*, **20**, pp. 565–567, 1910.

† Hallwachs, *Phys. Zeit.*, **5**, pp. 489–499, 1904; *Ann. d. Physik*, **23**, pp. 459–516, 1907.

plate enclosed in a glass vessel closed with a quartz window the period required was not less than 330 days. Such a cell can be used for the photometry of ultra-violet light.

The experiments of Aigner * on the fatigue of zinc led him to the conclusion that the influence of the vessel suggested by Hallwachs, if present at all, is very small. These experiments have been criticised by Hallwachs and Ullmann on the ground that the containing vessels were of such shape that the gases within could play but a small part in bringing about fatigue. All the vessels were narrow cylinders not more than 6 cm. in diameter, and differing only in length (from 25 to 150 cm.).

Ullmann † carried out an investigation on the influence of the size of the vessel on the fatigue of zinc, by which this effect was made certain. The vessels used were a 1-litre glass flask, a glass vessel of 600 litres, and a room of 9.4×10^4 litres. The mean percentage fatigue observed with these three vessels amounted to 27.4, 32.8, and 40.5 respectively. It was found that the transference of the plate under test from the vessel to the testing cell produced a certain amount of fatigue (not observed in the case of copper), which was allowed for by special experiments.

H. S. Allen ‡ also has observed a marked difference in the fatigue of zinc when that fatigue takes place in the air of a room and inside a closed testing vessel. In the confined space the fatigue proceeds more slowly; thus in one series of experiments the activity diminished 31 per cent. in 16 minutes inside the vessel, but in the air of the room 47 per cent. in the same time.

Ignorance of the influence of the size of the vessel on fatigue goes far to explain the contradictions found in the records of the earlier experiments on the subject.

The fact that the rate at which the fatigue proceeds diminishes with the size of the containing vessel is evidently of

* F. Aigner, *Akad. Wiss. Wien, Sitz. Ber.*, **115**, 2a, pp. 1485-1504, 1906.

† Ullmann, *Ann. d. Physik* (4), **32**, pp. 1-48, 1910.

‡ H. S. Allen, *Ann. d. Physik*, **32**, p. 1111, 1910; *Phil. Mag.*, **20**, p. 571, 1910.

fundamental importance when considering the cause of fatigue. Hallwachs suggests three hypotheses: (1) the fatigue is due to some substance present in the air in only small quantities; (2) the fatigue is due to some form of radiation which cannot penetrate the walls of the vessel; (3) the vessel prevents the escape of something (electrified particles or some form of radiation) from the plate under test. Hallwachs rejects the two last hypotheses, and attributes the fatigue principally to certain substances in the surrounding atmosphere. In the case of Cu and CuO water vapour produces a certain effect, but one that is too small to account for the fatigue observed; wood-tar gives a strong, ammonia a very strong effect; but, according to Hallwachs, the agent that is primarily responsible for photo-electric fatigue is ozone. In the case of zinc Ullmann finds that water vapour brings about marked fatigue both in air and in hydrogen, though here too ozone is effective in promoting fatigue. Another factor that is of influence in checking fatigue in a small vessel is the prevention of air-currents which would bring fresh amounts of the substance producing fatigue up to the metal surface.

3. *Does Fatigue take place in Gases other than Air?*—An answer to this question is likely to throw much light on the nature of the causes that bring about fatigue. It might be supposed, before any investigation had been carried out, that air or oxygen was essential for the production of fatigue. Thus Knoblauch,* who held the erroneous view that the photo-electric current is directly caused by the process of oxidation (see p. 83), explained the fatigue of a zinc plate as due to the formation of a layer of oxide.

It has been stated by some writers that fatigue does not take place in hydrogen. Thus Varley† records observations on zinc in hydrogen from which he infers that there is no sign of fatigue. On the other hand, Hallwachs‡ describes experiments with copper and platinum, which prove that the fatigue of these metals in hydrogen is quite analogous to

* Knoblauch, *Zeit. f. Phys. Chem.*, **29**, p. 257, 1899.

† Varley, *Phil. Trans. Roy. Soc.*, A, **202**, p. 444, 1903.

‡ Hallwachs, *Ann. d. Physik*, **23**, pp. 489-490, 1907.

that observed in air, the fatigue of copper being somewhat less rapid, but that of platinum being somewhat more rapid in hydrogen than in air. The fatigue of zinc in hydrogen has been established by the experiments of Ullmann* and of H. S. Allen.† The latter also examined the behaviour of aluminium and copper, and found that the fatigue took place at about the same rate in hydrogen as in air. In these experiments the metal plate was polished and put in position in the testing vessel, the air was displaced by a current of hydrogen, and observations of the activity were commenced a few minutes after polishing. It is not probable that the gas was entirely free from water vapour, nor is it likely that the air-film on the surface of the plate was immediately changed.

The influence of the surrounding medium on photo-electric activity was clearly shown in the researches of Wulf.‡ Chlorine and ozone were found to cause strong fatigue with a platinum electrode. With ozone the effect of moisture was particularly marked. With moist ozone the activity fell to half its initial value in 1 minute, while in dry ozone a similar diminution required about 15 minutes.

4. *Does Photo-electric Fatigue depend on the Electrical Condition of the Plate?*—In the experiments of Kreusler§ differences of potential not far short of those required to produce a spark were employed, but there is no evidence showing any effect on the process of fatigue due to these high potentials. In order to free the results from the effect of the fatigue, each series of observations was divided into two parts. The first gave the intensity of the photo-electric current in going from high to low potentials, the second in going from low to high. The results were plotted with the cathode potential as abscissa and the current intensity as ordinate. This gave two curves. The mean curve was drawn, and gave the relation for a constant activity. If a is the maximum ordinate of the descending curve and b the corresponding ordinate of the mean

* E. Ullmann, *Ann. d. Physik*, **32**, p. 33, 1910.

† H. S. Allen, *Ann. d. Physik*, **32**, p. 1111, 1910; *Phil. Mag.*, **20**, pp. 569-570, 1910.

‡ Wulf, *Ann. d. Physik*, **9**, p. 946, 1902.

§ Kreusler, *Ann. d. Physik*, **6**, p. 398, 1901.

curve, $\frac{a}{b}$ gives a measure of the fatigue effect. There is no indication of this ratio being dependent on the potentials employed.

E. v. Schweidler,* in studying the variations in photo-electric activity of zinc, aluminium, magnesium, and magnalium, found that the fatigue proceeds at the same rate whether the illuminated plate carries a positive or a negative charge.

Hallwachs† found no effect on the fatigue due to the electrical condition of the plate. He carried out a series of simultaneous observations on the photo-electric activity and the contact potential of a plate of copper. No parallelism was found between the fatigue effect and the variation of the contact potential. He concluded that the formation of double layers, as suggested by Lenard, could not be the main cause of the fatigue, though such a change might perhaps explain a certain percentage of the observed effect.

Sadzewicz‡ also found that the degree of fatigue does not depend on the initial value of the current, on the electric state of the plate during illumination, nor on its photo-electric sensitiveness. It is thus not an electric phenomenon properly so-called, and is not closely connected with Hallwach's phenomenon.

The variations in the contact difference of potential of zinc were found by Ullmann§ to have little or no influence on the photo-electric activity, so that it is not possible to explain the photo-electric fatigue of zinc as being caused by such variations.

H. S. Allen,|| too, showed that the rate at which fatigue takes place with a zinc plate does not depend on the strength of the electric field applied, nor on the sign of the charge on the plate.

* E. v. Schweidler, *Akad. Wiss. Wien. Ber.*, **112**, IIa, p. 974, 1903.

† Hallwachs, *Ann. d. Physik*, **23**, pp. 467-484, 1907.

‡ Sadzewicz, *Acad. Sci. Cracovie. Bull.*, **5**, pp. 497-498, 1907.

§ Ullmann, *Ann. d. Physik*, **32**, p. 46, 1910.

|| H. S. Allen, *Ann. d. Physik*, **32**, p. 1111, 1910; *Phil. Mag.*, **20**, pp. 568-569, 1910.

THE RATE OF PHOTO-ELECTRIC FATIGUE

Buisson * found that the photo-electric activity diminished according to the exponential law. Schweidler † gives a formula in which the activity at any instant is represented by

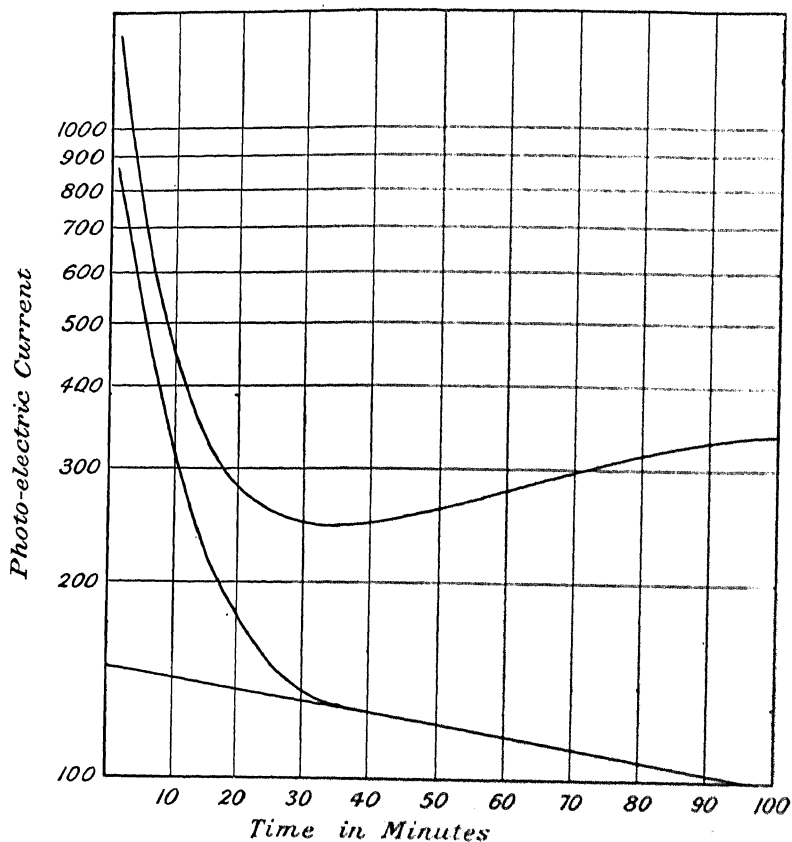


FIG. 34

the sum of an exponential and a constant term. H. S. Allen ‡ found in the case of polished and amalgamated zinc that two exponential terms were required. The diagram (Fig. 34)

* Buisson, *Annal. Chim. Phys.*, **24**, pp. 320-398, 1901.

† Schweidler, *Akad. Wiss. Wien, Sitz. Ber.*, **112**, 2a, pp. 974-984, 1903.

‡ H. S. Allen, *Proc. Roy. Soc., A*, **78**, pp. 483-493, 1907; **82**, pp. 161-164, 1909.

illustrates some of the curves obtained; the ordinate represents the logarithm of the photo-electric activity, the abscissa the time since the plate was polished. A straight line on the diagram would represent a single exponential term. He put forward the hypothesis that two consecutive changes took place at the surface of the zinc, but the nature of the modifications thus suggested was left an open question.

It is sometimes assumed that equations of the type here indicated necessarily refer to unimolecular changes. But in certain cases reactions are met with which, though really polymolecular, behave like unimolecular reactions.* Thus certain gaseous reactions take place on the surface of the walls of the containing vessel, and the velocity of the reaction is proportional to the pressure of the gas. The chemical change then appears as a reaction of the first order. A purely surface action may simulate the character of a unimolecular reaction.

Ramsay and Spencer † have published curves showing the "tiring" of metals when continuously exposed to light from a mercury vapour lamp. The curves they have obtained for magnesium, zinc, and tin show a number of breaks, the numbers corresponding to the number of valencies of the metal. In the case of aluminium at least five or six breaks were observed. No special precautions appear to have been taken to keep the source of light constant, and the curves of other observers do not show these breaks. In view of these considerations and other facts already brought forward, the theory that the metal undergoes a series of changes by the loss of "metallic corpuscles" cannot be maintained.

Anthracene shows photo-electric activity of nearly the same amount as that shown by zinc, and the activity decays with the time. The fatigue has been studied by A. Pochettino,‡ who finds that it can be represented by an exponential curve. The decay is observed only when the layer of anthracene exceeds a certain thickness (.02 mm.). The original activity

* H. M. Dawson, *Nature*, **71**, p. 532, April 5, 1905.

† Ramsay and Spencer, *Phil. Mag.*, **12**, p. 397, 1906.

‡ A. Pochettino, *Atti dei Lincei* (5), **15**, pp. 171, 355-363, 1906.

of anthracene which has completely lost its photo-electric properties can be restored, not only by leaving the material in darkness, but by exposing it for a few minutes to the radiation of radium. This case differs from that of the metals we are at present considering in the fact that the solid anthracene is a good insulator, so that the accumulation of surface charges probably accounts for the fatigue observed.

CONCLUSIONS

Reviewing the evidence brought forward as to the character of the change in the photo-electric fatigue of metal plates in gases, we see that certain of the theories proposed are ruled out as inapplicable. That the primary cause of fatigue is not oxidation is proved by the measurements of Hallwachs on the photo-electric activity of copper and its oxides, and by the results obtained in an atmosphere of hydrogen. Since fatigue is not directly due to the light, and since it depends on the size of the containing vessel, it cannot be due to a physical change of the metal itself or a disintegration of the metal. Again, the theory that fatigue is due to the formation of an electrical double layer is not in accordance with the experimental facts; contact difference of potential and photo-electric fatigue do not stand to one another in the relation of cause to effect, in fact they sometimes vary in opposite directions, and a large change in the potential difference is often accompanied by only a small change in the photo-electric activity. We must, then, conclude with Hallwachs that the main cause of photo-electric fatigue is to be found in the condition of the gaseous layer at the surface of the plate. This does not exclude the existence of secondary causes of fatigue in particular cases.

In the case of metals, such as copper, ozone plays a most important part in producing the rapid fatigue found in a large chamber. We must therefore inquire in what way the ozone affects the emission of electrons. Experiment showed that this action was not due to a special power of absorbing electrons possessed by ozone. In all probability it is due to the formation of hydrogen peroxide when the ozone

comes into contact with the metal plate. This substance absorbs ultra-violet light in a remarkable degree, and thus the presence of an extremely thin surface film is sufficient to account for the rapid diminution in the photo-electric activity experimentally observed.*

This explanation of photo-electric fatigue is in agreement with the facts observed in connection with changes in the contact difference of potential,† and with the production of an image on a photographic plate in the dark, when a metal plate is placed near to but not in contact with the sensitive film. It is capable also of explaining the results observed by Crowther,‡ who found that exposure to the α , β , and γ rays of radium produces a marked diminution in the photo-electric activity of a copper plate, while exposure to the β and γ rays only, produces much smaller fatigue.

PHOTO-ELECTRIC FATIGUE IN A VACUUM

If one reflects on the difficulties attaching to the preparation of a perfectly clean surface in a very high vacuum, it can occasion little surprise to find that contradictory conclusions have been reached as to the existence of photo-electric fatigue in a vacuum. These difficulties must be borne in mind in reading the following pages, in which an attempt is made to summarise the principal investigations bearing on this question.

In the experiments of Lenard§ the photo-electric current was measured in a high vacuum. An aluminium plate was freshly polished and immediately placed in the apparatus to be evacuated. The observations began when the pump had nearly reached the limit of its powers, about one hour after polishing the plate. The photo-electric activity at first showed a diminution lasting for about three-quarters of an hour—that is, about as long as the pump removed bubbles of gas from the apparatus. After that the activity remained unaltered over a period of ten days.

* Hallwachs, *Comptes Rendus du Congrès international de Radiologie et d'Electricité*, Brussels, 1910, p. 642.

† H. Beil, *Ann. d. Physik*, **81**, pp. 869–870, 1910.

‡ Crowther, *Camb. Phil. Soc. Proc.*, **14**, pp. 340–350, 1907.

§ Lenard, *Ann. d. Physik*, **8**, pp. 149–198, 1902.

In the case of a surface of lampblack, fatigue was observed even in a good vacuum. Freshly deposited surfaces were always most active; in the course of the first day there took place rapid, and later on slow decay of the activity; even after a stay of months in a vacuum the surface did not show a constant activity. In a long period a decay of the activity to about $1/7$ was observed. If air was admitted to atmospheric pressure and the vessel again exhausted, the activity showed an increased value. According to Lenard this points to the formation of an electrical double layer on the surface. At the end of a long series of experiments a picture of the gauze was found on the lampblack surface, the meshes of the gauze being lighter and the wires shaded darker. This suggests that in the carbon itself there is some alteration, which appears to be brought about by the light (see p. 5).

In the experiments of Ladenburg* fatigue was observed with metal surfaces in a highly exhausted vessel. The plates were polished with emery and oil. Aluminium proved an exception to the other metals examined, as no fatigue could be detected in this case. The fatigue was specially marked with a silver electrode,† but less prominent with platinum and copper. There appeared to be an alteration in the surface of these electrodes, as a peculiar veil was seen, from which it was concluded that the surface had been corroded by the action of the ultra-violet light. Electrolytically deposited surfaces of gold and nickel showed strong fatigue.

Several investigators have examined the behaviour of the alkali metals, either in hydrogen at a low pressure or in a good vacuum. Elster and Geitel‡ have used their potassium and sodium cells for photometric determinations, a proceeding which would have been impossible had not the activity been independent of previous illumination. Harms§ has employed a rubidium cell in a similar way. E. v. Schweidler,|| who

* E. Ladenburg, *Ann. d. Physik*, **12**, pp. 568-570, 1903.

† It is curious that Allen found no fatigue with a plate of pure silver when tested in a closed vessel in air or in hydrogen at atmospheric pressure.

‡ Elster and Geitel, *Wied. Ann. d. Physik*, **48**, p. 627, 1893.

§ Harms, *Phys. Zeit.*, **7**, p. 496, 1906.

|| E. v. Schweidler, *Phys. Zeit.*, **4**, p. 136, 1902.

carried out a series of experiments with a potassium cell, using an Auer burner as the source of light, states that no fatigue effects were observed after passing a photo-electric current through the cell for several hours. The passage of a glow discharge under a potential difference of 350 volts did, however, produce a diminution of photo-electric activity, possibly by changing the gas pressure in the cell, possibly by producing an alteration of the surface of the metal.*

Experiments to test the existence of fatigue in the case of the alkali metals have been carried out by K. Bergwitz.† The metals examined were potassium, sodium, and rubidium in glass vessels containing hydrogen at a pressure of 0.33 mm. No fatigue was observed when the metals were exposed to the light of a Nernst lamp or of an arc lamp at a distance of 1 metre, the heat rays being removed by filtering the light through cold water. The same result was obtained with the liquid alloy of potassium and sodium, whose surface can be renewed in a vacuum.

Slow photo-electric fatigue has been observed in the case of the alkali metals by H. Dember.‡ Two cells were prepared containing sodium in an atmosphere of carefully purified hydrogen. The first cell showed a diminution in activity of 7.6 per cent. after 30 days, and of 25.7 per cent. after 87 days. The second cell showed a diminution in activity of only 11.6 per cent. after 87 days. In these experiments the cells were only exposed to light when the test was made. An exposure of $1\frac{1}{2}$ hours to the light of a quartz mercury vapour lamp caused no measurable fatigue. This result was also obtained with NaK alloy in a cell provided with a quartz window. These results are taken as confirming the conclusions of Hallwachs that light is not the active agent, and that oxidation and corrosion are not responsible for the fatigue. The presence of ozone is here out of the question, but the fatigue

* Compare a similar observation by Elster and Geitel, *Wied. Ann.*, **52**, p. 439, 1894.

† Bergwitz, *Phys. Zeitschr.*, **8**, p. 373, 1907.

‡ Dember, *Phys. Zeitschr.*, **9**, pp. 180-190, 1908.

may be due to absorption of the hydrogen. The fatigue might then be attributed to an alteration in the gas pressure, since there is a critical pressure for which the current is a maximum.

In their experiments on the influence of temperature upon photo-electric effects in a high vacuum, Millikan and Winchester* found no evidence of fatigue effects in the case of either aluminium or silver. After 16 minutes' continuous exposure to ultra-violet light, the rate of discharge was practically unaltered. They conclude that "clean unpolished metals exhibit in a vacuum, under the influence of a given source, perfectly definite and constant discharge rates." They note, however, that if a particular disk† were illuminated continuously for three or four minutes, and a reading taken immediately thereafter, or if a large number of readings were taken in rapid succession, the results became irregular. This is attributed to a charging of the inner wall of the glass tube, because of the passage of some of the discharged electrons through the meshes of the wire gauze used to prevent electrostatic disturbances.

Attention must be drawn to the fact that the metals for these experiments were all polished on a wheel with dry emery, then washed in alcohol and dried by heating to 400° C. during exhaustion of the bulb. The vacuum was produced by a mercury pump of special design, and a McLeod gauge registered .00001 mm. of mercury or less.‡

Later experiments§ were made upon silver, zinc, iron, nickel, and copper in a very high vacuum. In no case was any positive evidence of photo-electric fatigue obtained.

* Millikan and Winchester, *Phil. Mag.*, **14**, pp. 188-217, 1907.

† Silver, iron, gold, brass, copper, nickel, magnesium, aluminium, antimony, zinc, lead were the metals employed.

‡ According to the experiments of F. S. Spiers (*Phil. Mag.*, **49**, p. 70, 1900), it is useless to attempt to drive off the last remnants of air from metal plates by merely heating them in a vacuum. "Even in a high vacuum of pure dry hydrogen at the minute pressure of 10^{-6} mm. of mercury, and after four washings in that gas, there is still sufficient oxygen present to completely oxidise the surface of an aluminium plate, if it only be brought to a sufficiently high temperature."

§ Millikan and Winchester. *Phys. Rev.*, **29**, p. 85, 1909; Millikan, *Phys. Rev.*, **30**, p. 287, 1910.

Continuous illumination by a powerful arc produced an *increase* in the photo-electric current to a maximum value, which remained constant even under the most prolonged illumination. In other experiments * in which mercury vapour was excluded from the tube the following values were obtained for the current before and after illumination of from ten to seventeen hours' duration :

Metal.	Current.	
	Before.	After.
Al	1.88	7.72
Pt	5.42	8.14
Steel	3.09	5.50
Cu	1.72	2.77
Zn	0.37	3.46
Au	0.28	1.85

The initial velocities were also increased by the illumination.

Interesting results have been obtained with regard to the fatigue of zinc and aluminium by J. Robinson.† The electrodes were polished by rubbing with steel, and inserted in a glass vessel which was pumped out to a high vacuum as quickly as possible. The experiments extended over some weeks, during which time the vacuum was constantly maintained. The plates were tested both by measuring the rate at which they charged up positively and by measuring the photo-electric current. Both metals showed fatigue after exposure to ultra-violet light ; by keeping the plates in darkness the original activity was regained after a few minutes. The important result was found that if the metal is kept at a positive potential so as to prevent the emission of electrons, no fatigue took place ; the metal is fatigued only when it gives off electrons. Robinson explains this by supposing that the electrons starting from some depth below the surface bring molecules of occluded

* Millikan and Wright, *Phys. Rev.*, **34**, p. 68, 1912.

† J. Robinson, *Phil. Mag.*, **23**, pp. 255-261, 1912.

gas to the surface. The surface film of gas hinders the emission of slow-moving electrons. When the plate is charged positively, there is no stream of electrons and no accumulation of gas. Recovery is due to the diffusion of the gas away from the surface of the metal.

K. T. Compton* has investigated the effect of photo-electric fatigue on the form of the velocity distribution curves. The metal plates were polished with chalk dust and afterwards tested in a vacuum. He believes that the shift of the curves with time (when the metal plates have received no abnormal treatment, such as making them the electrodes for an induction-coil discharge) can be accounted for by the time changes in the contact difference of potential between the emitting and receiving plates. Commenting on these results, Hallwachs† points out that when the velocity distribution curves are properly corrected in the manner proposed by Compton, the curves obtained after 1, 7, 21, and 31 hours fall upon one another. Although the aluminium plate under test is fatigued so as to show only one-third of its initial activity, yet the distribution of the initial energy amongst the electrons remains the same; in other words, the initial velocities are independent of the fatigue. This proves that alterations in double layers cannot be, as suggested by Lenard, a primary cause of fatigue, for the effect of such double layers would be to give smaller initial velocities with the fatigued plates.

To sum up the results of these investigations is not easy, since many of the results are contradictory. There is, however, considerable evidence to show that for the alkali metals there is no true fatigue. Many of the experiments on these metals have been made not in a high vacuum, but at a pressure somewhere near the critical pressure, and it is probable that the changes in activity actually observed are to be attributed to changes in the pressure. In the case of the other metals examined, it seems probable that in the case of a perfectly clean metal surface in a very high vacuum no fatigue would take place. The nearest approach to the realisation of such

* K. T. Compton, *Phil. Mag.*, **23**, pp. 579-593, 1912.

† Hallwachs, *Deutsch. Phys. Gesell. Verh.*, **14**, pp. 638-642, 1912.

a surface is afforded by the method of distillation in a vacuum worked out by Hughes. To explain the fatigue observed by some investigators, we must take into account the mode of preparation of the surface, the difficulty of removing surface films or gas occluded in the metal, and the possibility of changes in the gas pressure.

CHAPTER XIII

FLUORESCENCE AND PHOSPHORESCENCE

AN intimate relation exists between photo-electricity—that is, the separation of electrons under the influence of light—and the emission of light in fluorescence and phosphorescence. Although considerable progress has been made in the development of the theory of such emission in terms of the electron hypothesis, much work remains to be done before all the steps of the process are fully understood. In the present chapter we propose to indicate the bearing of the facts of photo-electricity already recounted on our conception of fluorescent and phosphorescent phenomena.

The term *luminescence*, proposed by Wiedemann, is a convenient one to include all cases in which there is an emission of light due to any stimulus other than heat. Different kinds of luminescence can be recognised, and may be classified according to the nature of the stimulus. Thus we may distinguish between *electro-luminescence*, due to such agencies as cathode rays, Röntgen rays, Becquerel rays, or canal rays; *tribo-luminescence*, due to friction or crushing; *chemi-luminescence*, due to chemical action; and *photo-luminescence*, due to the action of light.

In the various cases included under the heading electro-luminescence we can see at once that the excitation must be closely connected with the displacement or separation of electrons from the atoms of the substance. In tribo-luminescence again, if we bear in mind the facts of frictional electricity, we see that such displacement or separation of electrons must take place. In chemi-luminescence we may attribute the action to the rupture of a chemical bond (displacement of a valency electron). So, when we come to consider the cases included under photo-luminescence, it is

natural to suppose that the separation, either partial or complete, of electrons from the atom is an important stage in the process by which the emission of light is brought about. This is, briefly, the view of photo-luminescence which it will be our object to develop.

Luminescence which is observed during the time the stimulus acts is called fluorescence, but when the luminescence continues after the cessation of the stimulus it is called phosphorescence. It is scarcely possible to draw a hard-and-fast line between the two cases. Speaking generally, we may say that liquids and vapours may be fluorescent, but are not found to be phosphorescent, while all solids which show luminescence are phosphorescent. Without entering into a detailed description of the phenomena,* we may first briefly summarise the principal experimental results.

Probably the first recorded observation of fluorescence is that described in the fifth volume of the works of Boyle: "If you make an infusion of Lignum Nephriticum in spring water, it will appear of a deep colour like that of oranges when you place the vial between the window and your eye, and of a fine deep blue when you look on it with your eye placed between it and the window." Lignum nephriticum is the wood of a small Mexican tree or shrub. Sir David Brewster † observed the blood-red fluorescence produced by passing a beam of sunlight into an alcoholic solution of chlorophyll, and Sir John Herschel ‡ noticed the "beautiful celestial blue colour" shown by a solution of quinine "under certain incidences of the light." He remarked that the incident light lost the power of producing this effect after passing through a small thickness of the solution.

Sir George Stokes, who suggested the term fluorescence, made the first important investigation of these phenomena and introduced new methods of experimenting. By moving the substance under examination through the spectrum, he

* For such a description the reader may be referred to Kayser, *Handbuch der Spectroscopie*, 4, 1908.

† Brewster, *Trans. Roy. Soc. Edin.*, part 2, p. 3, 1846.

‡ Herschel, *Phil. Trans.*, p. 143, 1845.

found that the ultra-violet rays were in many cases specially active in causing luminescence. In the case of the solution of sulphate of quinine "it was certainly a curious sight to see the tube instantaneously lighted up when plunged into the invisible rays; it was literally *darkness visible*." By using Newton's method of crossed prisms he was able to compare the refrangibility of the incident light with that of the light emitted, and he enunciated the law that the wave-length of the fluorescent radiation is always longer than that of the radiation which excites the fluorescence. This law was called in question by Lommel. Investigations by a number of physicists have shown that as thus stated it is not universally true, and requires modification if it is to include all the cases observed. The law of Stokes has been qualified by Nichols* in the following way: "Luminescence is due to an absorption band. The absorption band and the luminescence spectrum overlap, and all waves included in the absorption band can produce excitation. . . . In luminescent bodies the maximum of intensity for a given substance is fixed as to wave-length and is independent of the intensity of excitation and of the character of the stimulus."

Fluorescence is shown by many organic liquids and by many solutions of organic salts. In the latter case the extremely small quantity of substance required is sometimes very remarkable. The amount of fluorescein or eosin in solution in optically transparent water when the fluorescence becomes invisible in daylight is 10^{-8} gm. per c.c., and is only 10^{-13} gm. per c.c. when the fluorescence is just visible at the apex of a concentrated beam from an arc lamp.† All aromatic compounds are said to fluoresce to some extent. The different nuclei (benzene, naphthalene, &c.) vary in their power of producing fluorescence. Some groups or "chromophores" ($-\text{NH}_2$, $-\text{OH}$, $-\text{COOH}$) increase the fluorescence, others ($-\text{NO}_2$, $-\text{Cl}$, $-\text{Br}$, $\text{C}_6\text{H}_5\text{CO}-$, $(\text{CH}_3\text{CO}-)$) diminish it.‡

Phosphorescence—luminescence which continues for a cer-

* Nichols and Merritt, *Phys. Rev.*, **19**, p. 409, 1904.

† W. Spring, *Bull. Acad. Roy. Belg.*, pp. 201-211, 1905.

‡ Francesconi and Bargellini, *Accad. Lincei, Atti*, **15**, pp. 184-191, 1906.

tain period after the stimulus has ceased to act—is found in a large number of solids. It is supposed to occur only in a *solid solution*. Pure bodies are commonly regarded as incapable of showing phosphorescence, though, as in the phosphorescent preparations made by H. Jackson,* the amount of impurity may be far too small to be detected by the ordinary methods of chemical analysis.† In a binary system the brightness and position in the spectrum of a phosphorescent band depend on the relative proportions of the two substances, the greatest effect corresponding to a relatively small proportion of the substances producing phosphorescence. The sulphides of calcium, strontium, and barium are noteworthy amongst phosphorescent substances, Balmain's luminous paint being composed of these sulphides. Dewar‡ found that many bodies which show only feeble traces of phosphorescence at ordinary temperatures show a very marked effect at the temperature of liquid air. When the duration of the phosphorescence is short it may be measured by means of the phosphoroscope of Becquerel or that of Lenard.

The spectrum of the fluorescent or phosphorescent light has been examined by very many observers. In general a banded spectrum is obtained, each band showing a maximum of intensity at a definite point in the spectrum. According to Lenard the bands of phosphorescence are of a very complex structure, which suggests that we have really to deal with a number of overlapping bands.

Very remarkable results have been obtained by R. W. Wood§ from a study of the fluorescence of the vapour of sodium and of other substances. In such cases a line spectrum of a complicated character is observed. There appear to be groups of lines in the spectrum of the fluorescent light, which can only be excited by radiation of a definite wavelength. An independent examination of mercury vapour by

* H. Jackson, *Phil. Mag.*, **46**, p. 402, 1898.

† L. Bruninghaus, *Annal. Chim. Phys.*, **20**, pp. 519–546, **21**, pp. 210–283, 1910.

‡ Dewar, *Proc. Roy. Inst.*, **14**, p. 665, 1895.

§ R. W. Wood, *Phil. Mag.*, **10**, p. 251, 1905; *Phys. Zeit.*, **10**, pp. 425, 466, 1909; *Physical Optics*, chapter XX, 1911.

W. Steubing* showed that the absorption of light by the ultra-violet bands of short wave-length resulted in the emission of fluorescent light by the series lines λ 2536 and λ 2346.

At extremely low temperatures the spectrum of phosphorescent light consists of very fine lines instead of broad bands. The uranyl salts show luminescence spectra which at ordinary temperatures consist of a group of several bands, whose arrangement suggests the banded spectra of gases. These have been examined at low temperatures by H. and J. Becquerel and Onnes. If a curve is plotted showing the relation of the intensity to the wave-length of the light, not only each component band, but the envelope of the group of bands, is found to be of the same type as the curve of distribution of energy in ordinary fluorescence bands. Further, these curves resemble, though with very different scales of wave-length, the energy curve of the temperature radiation of a black body.

THEORIES OF FLUORESCENCE AND PHOSPHORESCENCE

All attempts to formulate a theory of fluorescence or phosphorescence must be based on the work of Stokes, who first clearly recognised that in fluorescence there was a transformation of the incident radiation into radiation of a different refrangibility. In his lectures *On Light* (p. 150) he writes: "The view which I have all along maintained is that the incident vibrations caused an agitation among the ultimate molecules of the body, and that these acted as centres of disturbance to the surrounding ether, the disturbance lasting for a time which, whether it was long enough to be rendered sensible in observation or not, was at any rate very long compared with the time of a single luminous vibration."

A satisfactory theory of photo-luminescence must distinguish between absorbing media which exhibit luminescence and those which do not; secondly, it must give an explanation of the law of Stokes; and thirdly, it must account for phosphorescence in solid substances with its peculiar tem-

* W. Steubing, *Phys. Zeit.*, 10, p. 787, 1909.

perature relations. These requirements cannot be met by a theory of simple resonance.

The most serious attempt to explain fluorescence as a resonance phenomenon was that made by Lommel.* He assumed that the atoms of the illuminated substance which were set in vibration by the incident light were subject to damping through friction proportional to their velocity, and were under the action of a restoring force proportional to the square of their displacement. In consequence the free and forced vibrations must be accompanied by the overtones.† Absorption of energy may take place through resonance, either in the case of the fundamental vibration or in the case of an overtone. The vibrations set up by resonance immediately give rise to the emission of fluorescent light. Now, in order that the kinetic energy of a vibrating system should be a maximum through resonance, the frequency of the impressed force must be equal to that natural to the system *if friction were absent* (Eigenfrequenz)—that is, it must be greater than that natural to the system with friction.‡ Thus, if we suppose that the fluorescent light is emitted by the system when vibrating with its natural period, we see that the frequency of the exciting light is greater than that of the fluorescent light. This is the law of Stokes. The theory, however, would point to all absorption being accompanied by fluorescence, and the damping coefficients required are not in harmony with experiment. It is now generally agreed that the difficulties to be faced by such a theory are insuperable, both from the theoretical and from the experimental side.

The difficulties met with in regard to Lommel's theory prove that the supposition of resonance is not by itself sufficient to explain fluorescence; it is therefore necessary to make further hypotheses to aid in the explanation. Wiedemann and Schmidt§ introduced the hypothesis that the fluorescing molecule could exist in several conditions. Thus under

* Kayser, *Handbuch der Spectroscopic*, 4, pp. 1078–1088, 1908.

† Rayleigh, *Theory of Sound*, 1, pp. 76–77, 1894.

‡ Barton, *Text-Book of Sound*, chapter IV; J. P. Dalton, *Nature*, 89, p. 528, 1912.

§ Wiedemann and Schmidt, *Ann. der Physik*, 56, p. 246, 1895.

the influence of the absorbed light a transformation may take place from a state A to a state B. Fluorescence may occur either in the transformation from A to B, or in the retransformation from B to A. The transformation in question may be either a chemical change in the usual sense, or a change within the molecule, or an ionisation which may result in an action between the ions and the surrounding medium. Expressed in this way the theory is very general in character, and will be found to include many suggestions put forward by others (Kauffmann, Baly, Hewitt, Armstrong). It has been supported by Nichols and Merritt,* who hold that excitation produces electrolytic dissociation of the active substance, and that the resulting luminescence arises from vibrations set up in the processes of dissociation or association of the ions.

The theory of Voigt presents some points of resemblance to that of Wiedemann and Schmidt. He supposes that the molecules of a fluorescent body resemble to a certain extent the molecules of a partially dissociated gas, in that they can exist in two or more different conditions, differing in their electron configuration. Taking two conditions, A and B, it is assumed that in unit time the change from A to B takes place as often as the change from B to A. The period corresponding to A is T_A , that corresponding to B is T_B . If light of period T_A is incident, A is set in vibration with that period. But A suddenly changes to B. Free vibrations of this system then take place with period T_B , and these vibrations are supposed to be damped. Voigt assumes that the state with the longer period B experiences very much smaller damping than A. In this case the absorption of B will be small compared with that of A, and, on the other hand, the emission of A will be small compared with that of B. In this way he avoids the difficulties of having to deal with two absorption bands and two fluorescence bands.

As Kayser has pointed out, all these theories rest on the same supposition that on excitation a stable form is changed by the reception of energy into a labile form. The retrans-

* Nichols and Merritt, *Phys. Rev.*, **27**, pp. 367-399, 1908.

formation into the stable form takes place with an emission of energy in the form of light, but against a resistance whose magnitude is a function of the temperature. The various theories differ only in that they assume a transformation into isomeric modifications or other molecular complexes, or into ions, or finally into ions or electrons, and in that they regard the resistance as mechanical or electrical in nature. From the standpoint of this book we are concerned with the expression of these theories in terms of electrical actions.

Further progress in the study of luminescence is closely associated with the development of our knowledge of the general problem of the emission of radiation, and the description of the processes of such emission in terms of the electron theory.

According to the view developed by J. J. Thomson,* luminosity in a vacuum tube discharge accompanies ionisation, and the ionisation may be due to the internal energy of the atom rising to such a value that the equilibrium becomes unstable and a kind of explosion occurs, resulting in an expulsion of corpuscles. The passage from the dark to the luminous discharge takes place very abruptly, and this suggests that the luminosity sets in when that part of the internal energy of the atom which gives rise to the particular kind of light present attains a perfectly definite value. The critical amount of energy is dependent upon the character of the light emitted.

Kowalski † has based on this a theory of luminescence. He considers that every phosphorescent body contains two distinct systems of electron groupings—"electronogens" and "luminophores." The former expel electrons under the action of the stimulus. In fluorescence the latter shine out *only* while the electrons from the former are traversing them. Phosphorescent bodies *gradually* radiate out energy till the energy of the luminophores is reduced below the critical value necessary for the production of light.

* J. J. Thomson, *Nature*, **73**, pp. 495-499, 1906.

† Kowalski, *Phil. Mag.*, **13**, p. 622, 1907; *Acad. Sci. Cracovie, Bull.*, **8**, pp. 649-764, 1908.

This theory certainly contains elements of truth, but it does not afford such a clear description of the processes involved in luminescence as that which has been given by Stark, or that given by Lenard for phosphorescence. These theories we proceed to consider in greater detail.

STARK'S THEORY OF LUMINESCENCE *

According to Stark's view there exists at the surface of the atom a limited number of separable electrons which play the part of valency electrons—that is, they serve to bind together the chemical atoms in a molecule by the electrical forces exerted. A valency electron may be completely separated from its atom and become attached to a second atom. The first atom in this way assumes a positive, the second a negative charge, and we thus obtain a positive and a negative atomion. Stark supposes that band spectra are characteristic of the valency electrons, so that the electromagnetic field of the valency electron may be regarded as the elementary oscillator of the band spectra. Thus the carrier of a band spectrum is a single atom or a molecule composed of several atoms. The vibrations of the oscillator may be excited by the recombination of positive atomions with negative electrons. The consequences deduced from this hypothesis as to the carrier of the band spectrum are found to be in good agreement with the results of observation.

The determination of the elementary oscillator in the case of the series or line spectrum is a more difficult problem. Stark supposes that the carriers of the series spectra are positive atomions—that is, single atoms which have lost one or more valency electrons. One consequence of this hypothesis must be that the series lines in the canal rays must show a Doppler effect. Although the interpretation of observations on canal rays is rendered difficult by the complex character which J. J. Thomson has shown these rays to possess, Stark holds that his hypothesis is supported by the experimental results. If the series spectrum appears when an atom has lost a valency electron, the seat of the emission

* J. Stark, *Prinzipien der Atomdynamik*, II, pp. 213-227, 1911.

and absorption is probably that portion of the atom from which the valency electron has been separated. Stark assumes that the atom contains positively charged entities which he calls archions, and he is thus led to regard the elementary oscillator of a series spectrum as that archion, or those archions, from which the valency electron has been removed.

Seeing that no satisfactory explanation of the production of a fluorescent line spectrum has yet been given, it does not appear necessary to consider this part of Stark's theory in greater detail. We pass on to the consideration of a luminescent band spectrum, for in this case considerable progress has been made towards a complete explanation. Emission in band spectra is supposed to occur when valency electrons which have been partially or totally separated are restored to the atom. The process by which the separation has taken place is immaterial, so far as the character of the emission is concerned. But, according to Stark, the valency electrons may be identified with the photo-electric electrons, so that one process by which separation of valency electrons may be brought about is the photo-electric action of Hertz and Hallwachs. Fluorescence or phosphorescence in band spectra is that emission of light which accompanies the restoration of valency electrons in this case.

The difference between fluorescence and phosphorescence is not fundamental, it depends only on the time during which the separation of the electron continues. While in the case of fluorescence restoration follows immediately upon separation, in the case of phosphorescence a finite time elapses between the separation of a valency electron and its return, this interval of time differing for different electrons in the phosphorescent material. Though fluorescence is generally accompanied by the photo-electric effect, this is not essential, as the separation of the electron may be only partial. On the other hand, phosphorescence implies complete separation—that is, photo-electric emission. The duration of fluorescence is practically identical with the period of excitation on account of the small mass and correspondingly great reaction velocity of the electrons.

Stark and Steubing* have studied a large number of organic compounds from the point of view of this theory. In Table I of their paper they give a list of 37 benzene derivatives (without chromophores) showing the character of the fluorescence and the photo-electric activity. Those which fluoresce are photo-electrically active, though in a few cases the photo-electric effect could not be measured in consequence of the vapour given off from the volatile liquid. In general the photo-electric activity is greater the more intense the fluorescence. A case of special interest is that of benzene itself, which was known to have strong absorption bands in the ultra-violet, and on examination was found to possess bands of fluorescence also in the ultra-violet.† In Table III of the paper by Stark and Steubing similar results are recorded for 17 benzene derivatives with chromophores. These all show photo-electric activity, but the fluorescence is in some cases masked by the presence of the chromophore. This occurs when the absorption spectrum of the chromophore coincides with the fluorescence spectrum of the benzene derivative. Such a case of latent fluorescence is found with anthraquinone.

The authors point out that G. C. Schmidt‡ failed to establish a relation between fluorescence and photo-electric activity in consequence of the fact that many of the substances were tested in solution and not in the pure state. Such tests do not prove that the substance is photo-electrically inactive, as the separated electrons are caught by the molecules of the solvent and are less likely to escape into the surrounding space. The photo-electric effect becomes latent.

The theory of Stark affords an explanation of the fact that the fluorescent light from an anisotropic body is unpolarised even when the exciting light is polarised, and also of the fact that the wave-length of the fluorescent light differs from that of the exciting light. Einstein§ has given an explanation of the law of Stokes from the point of view of the unitary theory of light, which applies for this theory.

* Stark and Steubing, *Phys. Zeitschr.*, **9**, pp. 481-495, 661-669, 1908.

† J. Stark, *Phys. Zeitschr.*, **8**, pp. 81-85, 1907.

‡ G. C. Schmidt, *Ann. d. Physik*, **64**, pp. 708-724, 1898.

§ Einstein, *Ann. d. Physik*, **17**, p. 144, 1905.

If the frequency of the exciting light, whose energy is absorbed by the fluorescent substance, be ν_a , the elementary carriers of energy have the magnitude $zh\nu_a$, or, taking z in general as unity, $h\nu_a$. If this energy be imparted to the electron, the energy available for emission in the process of restoration cannot exceed $h\nu_a$, but can only be diminished by division. Hence the relation between the frequency, ν_f , of the fluorescent light and that of the exciting light must be of the form $h\nu_f \leq h\nu_a$, so that $\nu_f \leq \nu_a$, or $\lambda_a \leq \lambda_f$. Thus in general the wave-length of the exciting light is smaller than that of the fluorescent light. The fact that the fluorescent spectrum in some cases shows a small intensity for wave-lengths smaller than λ_a can be explained either by supposing that several energy quanta are absorbed by a single electron, or that the energy absorbed can be increased by an addition from the thermal kinetic energy of the molecules.

Stark divides the bands in the spectrum of a substance into two classes, which he calls short-wave and long-wave bands. In the former, both in absorption and in emission, the intensity diminishes in passing from shorter to longer wave-lengths; in the latter, the intensity diminishes in passing in the opposite direction. He supposes that the short-wave and the long-wave bands of a valency electron are dynamically coupled together in such a way that the emission of light with the frequency of a short-wave band is necessarily accompanied by a simultaneous emission of light with the frequency of the long-wave band. Both fluorescence and the photo-electric effect are intimately connected with those absorption bands which are shaded towards the red; when light is absorbed in such a short-wave band it brings about fluorescence both in this and in the coupled long-wave band. On the other hand, the absorption of light in a long-wave band which is shaded towards the ultra-violet is accompanied neither by fluorescence nor by the photo-electric effect.

From the point of view of the chemist, who is concerned with the relation between the constitution of the molecule and its power of fluorescing in a particular region of the spectrum, the practical problem reduces to the determination

of the relation between chemical constitution and the absorption spectrum. From the point of view of the physicist much work remains to be done in the investigation of the dynamics of the vibrations of the valency electrons.

LENARD'S THEORY OF PHOSPHORESCENCE

Experiments on the phosphorescent alkaline earths led Lenard and Sacland* to connect the phosphorescence with the photo-electric activity of the material. Such substances are usually good insulators, and when they emit electrons under the influence of light, they acquire a positive charge, which tends to neutralise the external field applied with a view to measuring the photo-electric current. This charge is not distributed over the whole surface exposed to the light, but is localised in particular regions. This can be explained by assuming that the photo-electric effect is confined to certain molecular groups or "centres." Under the influence of the light electrons are thrown off from the metal atoms of the centres, and these centres thus acquire a positive charge. The liberated electrons may be captured by the sulphur atoms, or they may be scattered amongst the surrounding atoms without becoming attached. The origin of the phosphorescence is to be found in the recombination of the centres and the electrons, whenever that recombination takes place. To this extent Lenard's theory resembles that of Stark, but Lenard distinguishes between the photo-electric electrons and the emission electrons. He holds that when the former return to the atom, the latter are brought into a state of vibration, and consequently emit radiation. By this theory the temperature relations of phosphorescence can be accounted for,† and the law of Stokes can be explained.

We consider first the variation of phosphorescence with temperature. From the study of the phosphorescent sulphides

* Lenard and Sacland, *Ann. d. Physik*, **28**, pp. 476-502, 1909.

† Nichols and Merritt, however, find a more complicated set of phenomena than can be directly accounted for by Lenard's hypotheses (*Phys. Rev.*, **32**, pp. 38-53, 1911).

Lenard* concludes that for each band in the spectrum of a body excited to phosphorescence there is a certain range of temperature within which it is phosphorescent, and above and below which no phosphorescence of long duration occurs, although fluorescence may be present both at higher and lower temperatures. Within the specified range electrons become attached to the sulphur atoms, but from time to time individual electrons escape and return to the centres where recombination, followed by luminescence, ensues. At very low temperatures, however, the sulphides of the alkaline earths are almost perfect insulators, consequently phosphorescence cannot ensue until the temperature is raised sufficiently for the substance to acquire a certain electrical conductivity. Thus at the temperature of solid hydrogen all the bands of the alkaline earth sulphides are brought into the cold phase, and show no lasting phosphorescence, but only a momentary luminescence.

The effect of an increase of temperature is held to be a shaking-up of the atoms, so that the frequency of collisions is increased and the return of the electrons is facilitated. The action of infra-red radiation is supposed by Lenard to be similar in character. Red and infra-red radiation set in motion the larger aggregates through resonance. These aggregates consist of sulphur atoms with the attached electrons; their free period is large, so that they respond to long waves. The increase in the number of collisions brought about by a rise of temperature or the incidence of radiation of long wave-length augments the phosphorescence, and at the same time makes the decay of phosphorescence more rapid. Thus with an increase of temperature the luminescence assumes more nearly the character of fluorescence, and when the temperature is sufficiently raised, no lasting phosphorescence is observed. On the other hand, substances which only fluoresce at ordinary temperatures may be made to phosphoresce by a considerable diminution of temperature. Thus

* Lenard and Klatt, *Ann. d. Physik*, **15**, pp. 425, 525, 633, 1904; Lenard, Kamerlingh Onnes and Pauli, *Konink. Akad. Wetensch. Amsterdam*, **12**, pp. 157-174, 1909.

all alkaloids forming fluorescent solutions become phosphorescent at low temperatures.

Lenard * explains the law of Stokes in the following way. When the photo-electric electron returns to the atom it is set in vibration with an amplitude that is at first large but afterwards diminishes. Now it is generally found that the period of a vibration diminishes as the amplitude diminishes. The excitation of the emission electrons by resonance will only take place when the period of vibration of the photo-electron has become identical with that of the emission electron. Thus the photo-electron can only bring about emission when it has finally a smaller period of vibration in the atom than the emission electron. This implies that the wave-length of the exciting light, which brings about the release of the photo-electron, must be less than the wave-length of the phosphorescent light.

From observations on about 50 phosphorescent aggregates made by the addition of a trace of a metallic salt to a sulphide of strontium, barium, or calcium, Lenard † was led to distinguish between three different processes in the decay of phosphorescence. One is a short or evanescent process (*m*-process, Momentanprozess) which obeys a logarithmic law of decay. This temporary effect is observed when the phosphorescent surface is exposed only a short time, say a few seconds, to the spectrum. The second is a more lasting process (*d*-process, Dauerprozess), in which the intensity of the light varies inversely as $(a + bt)^2$, where *t* is the time since excitation. This is obtained by an exposure of several minutes to the exciting light. It is also well shown after exposure to slow cathode rays. The third process is of medium duration, and is brought about principally by the action of ultra-violet rays (*u*-process). The short-lived luminescence can be produced independently of the longer-lived phosphorescence, not only by very brief excitation, but also by using portions of the ultra-violet which are incapable of exciting the *d*-process, or by working at temperatures above or below the range within which the latter process can occur.

* Lenard, *Ann. d. Physik*, **31**, pp. 675-677, 1910. † *Ibid.*, p. 641, 1910.

The decay of phosphorescence can be represented in many cases by means of the formula

$$I = \frac{a}{(c + at)^2}$$

where I denotes the intensity of the light, t the time, and a and c are constants. Lenard's theory affords an explanation of this relation, which applies to the d -process, in the following way. On excitation the photo-electric electrons are supposed to be detached from the metal atoms and to become attached to the neighbouring sulphur atoms. We may imagine that the excitation of the phosphorescent substance has been brought about at a low temperature. If the temperature is raised, the electrons will be released from the sulphur atoms and return again to the metal atoms, and in so doing bring about luminescence. The intensity of the light will be proportional to the number of electrons returning in unit time, *i.e.* to $\frac{dn}{dt}$, where n is the number of electrons attached to the sulphur atoms or wanting in the metal atoms. The force attracting the oppositely charged particles (S atoms and metal atoms) will be proportional to n^2 . Assuming that the action tending to restore electrons to the metal atoms is proportional to this force, we have $-\frac{dn}{dt} = an^2$, so that $n = \frac{1}{c + at}$ and $I = \frac{a}{(c + at)^2}$.

The short-lived phosphorescence (m -process) obeys a different law. In this case the separated electrons, instead of becoming attached to sulphur atoms, are distributed in the surrounding space like the molecules of a gas. The number of atoms returning in unit time to a metal atom will now be proportional to the number of collisions between electrons and metal atoms, *i.e.* to n . Thus $-\frac{dn}{dt} = an$, and therefore $I = I_0 e^{-at}$.

Such a relation has been found experimentally by E. Becquerel,* but a somewhat more complicated relation has been obtained in the experiments of Werner †—viz. $I = I_0 e^{-at^m}$

* E. Becquerel, *La lumière*, I, p. 273, 1867.

† Werner, *Ann. d. Physik*, 24, pp. 164-190, 1907.

where m is a number varying in different cases between the values 0.2 and 1. Lenard supposes that this is due to the complications brought about by the u -process, which is superposed on the m -process.

A further study of Lenard's phosphorescent preparations has been carried out by Pauli,* with a view to examining the effect of the solvent (sulphide) on the phosphorescence. By modifying the dielectric constant it was found possible to alter the position of the luminescent band at will, and Pauli was successful in preparing material which showed bands only in the ultra-violet, and other material showing bands only in the infra-red. The results obtained afford a striking confirmation of Lenard's view that the vibrations set up in the phosphorescent substance are analogous to those of an electric oscillator whose period depends upon inductance and capacity, and that the wave-length of a band is consequently proportional to the square root of the dielectric constant of the medium.

The case of phosphorescent zinc sulphide, which Lenard classes among the phosphorescent alkaline earth sulphides, has been examined by Ives and Luckiesh.† They find that the zinc sulphide exhibits a flashing-up of luminosity when radiation of long wave-length is incident upon it. The peculiarity of the effect in this case is that it becomes noticeable only after the decay of phosphorescence has proceeded for some time. The authors attempt to develop a theory of this effect based on the theory of Lenard. The initial direction of the decay-curve is ascribed to the unattached electrons, which bring about the rapid drop in luminosity in the early stage of the decay. The flashing-up is attributed to the stored-up electrons, which determine the shape of the decay curve in its later stages.

An interesting relation suggesting the possibility of a connection between phosphorescence and the *selective* photo-electric effect has been pointed out by Pohl.‡ Lenard found that corresponding to an emission band of a phosphor of the

* Pauli, *Phys. Zeitschr.*, **11**, p. 991, 1911.

† Ives and Luckiesh, *Astrophysical Journal*, **34**, pp. 173-196, 1911.

‡ Pohl, *Verh. Deutsch. Phys. Gesell.*, **13**, pp. 961-966, 1911.

alkali earths there were three separate bands which could produce excitation. It appears that the wave-lengths of these bands are inversely proportional to the square roots of the natural numbers 2, 3, and 4. Now, according to the formula of Lindemann (p. 149), the wave-length for the maximum selective photo-electric effect is inversely proportional to the square root of the valency. Thus there is a striking point of resemblance between the two sets of phenomena, but it would not be justifiable, without further investigation, to assume that phosphorescence is always associated with the selective rather than with the normal photo-electric effect.

THERMO-LUMINESCENCE

The term *thermo-luminescence* is employed in speaking of substances in which an emission of light is produced by a rise of temperature, though this temperature is far below that required for the ordinary thermal emission. Certain varieties of fluor-spar (chlorophane) exhibit this phenomenon in a very marked degree. Such cases really belong to the class of phosphorescent substances, as it is found that a preliminary exposure to light is necessary. E. Wiedemann* obtained the same effect by exposure to kathode rays. These phenomena may be compared with those recorded by Dewar,† in which substances exposed to light at the temperature of liquid air show no phosphorescence until they are warmed.

According to Lenard's theory, the electrons liberated by photo-electric action must become attached to neighbouring molecules in a fairly stable fashion, so that they are unable to effect their return to the parent atom until the vibration of the molecules is sufficiently increased by a rise of temperature. This explanation is supported by the observations of G. C. Schmidt,‡ who found that, in the case of solid solutions such as those examined by Wiedemann, thermo-luminescence and photo-electric sensitiveness were invariably associated if either of these properties were strongly marked.

* E. Wiedemann, *Wied. Ann. der Physik*, **56**, p. 201, 1895.

† Dewar, *Chem. News*, **70**, p. 252, 1894.

‡ G. C. Schmidt, *Ann. der Physik*, **64**, pp. 708-724, 1898.

CHAPTER XIV

PHOTO-CHEMICAL ACTIONS AND PHOTOGRAPHY

It is well known that there are numerous cases in which chemical changes are brought about by the action of light. We may conveniently divide such photo-chemical reactions into three main classes.* To the first class may be assigned the so-called *photokatalytic* reactions, in which light only accelerates an irreversible process. In such cases we cannot regard the energy of the light as being stored up in the transformed substance in the form of chemical energy. To the second class belong the true photo-chemical equilibria. These are processes in which a new state of equilibrium is set up under the action of light. This class is characterised by the fact that the processes concerned are fully reversible—that is, the whole system returns in the dark to its original condition. The energy of the light is transformed and accumulated in the form of chemical energy. To the third class belong the so-called false chemical equilibria. These are at bottom irreversible processes, which are composed of two or more photokatalytic reactions.

As we have seen in previous chapters, J. Stark identifies the valency electrons, which play the part of chemical bonds, with the photo-electric electrons which can be liberated by the action of light. From this point of view a photo-electric change and a photo-chemical change may be regarded as changes of the same character, consisting essentially in the displacement or separation of an electron through the absorption of energy from a light wave. Stark is thus led to distinguish between two kinds of photo-chemical action. In a primary or direct action the same valency electron which

* Johannes Plotnikow, *Photo-chemie*, W. Knapp, 1910; *Photochemische Versuchstechnik*, Akad. Verlagsges. Leipzig, 1912.

has absorbed energy is itself released from its connection with a strange atom, whilst in a secondary or indirect action the electron which has absorbed the energy causes by collision the separation of a neighbouring valency electron from an atom. Thus in either case the action results in the dissociation of a chemical bond.

The laws governing photo-chemical changes have been studied by many scientific workers, both from the point of view of chemistry and from that of physics. The law of Grotthus* is found to apply in all cases—only such rays can act chemically on a substance as are absorbed by it. But it does not follow that each type of radiation absorbed must produce chemical action. In connection with primary photo-chemical reactions J. Stark† enunciates three laws. First, these reactions are unimolecular. Second, they are independent of the temperature, at any rate for light of wave-length $450\text{ }\mu\mu$. Third, the amount of the product of reaction formed in unit time is proportional to the amount of the active light absorbed. This last law is that known as the law of Bunsen and Roscoe. It has been confirmed by the exact measurements of Wildermann.‡

From the point of view of modern physics we may regard it as practically certain that the first stage in any photo-chemical reaction consists in the separation, either partial or complete, of negative electrons under the influence of light. This view at once enables us to understand certain of the laws which are found to hold in photo-chemical reactions. It is obvious that absorption of light is necessary before any change can be brought about. When the light absorbed is able to effect the separation of electrons, then in unit time a definite number of molecules will lose electrons, the number being proportional to the intensity of the light and to the surface illuminated, but being independent of temperature. Thus we regard the action of the light as similar in character to its action in producing the photo-electric discharge, but whereas

* Luther, *Z. W. P.*, III, 7, p. 257, 1905; Lehmann, *Zeit. Phys. Chem.*, 64, pp. 89-119, 1908.

† J. Stark, *Phys. Zeitschr.*, 9, pp. 889-894, 1908.

‡ Wildermann, *Phil. Trans. Roy. Soc., A*, 199, p. 337, 1902.

in the latter case we have an emission of electrons with definite velocity, in the former we suppose that the separated electrons (valency electrons) in general attach themselves to some other atom or group of atoms. This hypothesis serves as a basis for the explanation of the laws of photo-chemical change.*

Our knowledge of the structure of the atom and of the mechanism of these changes is not yet sufficiently complete to enable us to form a perfectly clear mental picture of the processes involved, but there can be no doubt that work on the lines indicated in the previous chapters will do much to enable us to construct a model for the elucidation of such transformations. It may serve a useful purpose if we now refer to some of the most interesting photo-chemical changes, paying special attention to any facts that appear to be suggestive from our theoretical standpoint.

The most important chemical change brought about by light is that which occurs in the case of the chlorophyll of green leaves. Here there is a transformation of carbon dioxide into sugars and starch, involving the absorption of a very large amount of energy; in order to produce one gramme of starch from carbon dioxide and water, 4230 calories of energy must be supplied. According to the measurements of Brown and Escombe † nearly 100 per cent. of the light-energy absorbed is utilised, under favourable conditions, in bringing about chemical change. The unique character of the process is shown, not only in the large amount of energy absorbed, but in the fact that the maximum photo-chemical activity is in the red between the lines B and C, a part of the spectrum which is usually without photo-chemical action. There is a secondary maximum in the case of chlorophyll in the blue

* W. D. Bancroft, *Journal of Physical Chemistry*, **12**, pp. 200, 278, 318-176, 417-447, 1908, has discussed photo-chemical actions at length in a series of articles on the Electro-chemistry of Light, and has come to the conclusion that the theory put forward by Grotthus accounts for all the actions of light upon salts. According to this theory "the action of a ray of light is analogous to that of a voltaic cell," that is, the chemical action of light is essentially electrolytic in nature. This conclusion is in excellent agreement with the view here put forward, if the electrolytic dissociation is regarded as equivalent, at least in its first stage, to the separation of negative electrons under the influence of light.

† Brown and Escombe, *Proc. Roy. Soc., B*, **76**, pp. 29-111, 1905.

near F, and a minimum in the green corresponding with maximum transmission.

A theory of the mode of action of chlorophyll has been put forward by Harvey Gibson.* According to this theory the light rays absorbed by chlorophyll are transformed by it into electric energy, and this transformed energy then brings about the decomposition of carbonic acid (H_2CO_3) in the cell, with the concomitant formation of an aldehyde and the evolution of oxygen. From the aldehyde are derived the sugars and starch of the plant. The theory thus stated falls into two parts: first, a somewhat vague statement as to the transformation of light energy into electric energy; and second, a suggested chemical change. With the second process we are not here primarily concerned, but with regard to the first we may point out that an acceptance of the electromagnetic theory of light necessarily implies a transformation of the energy of the electromagnetic waves into the energy of electrified particles when absorption of light takes place. Whether the energy in this case consists in the energy of emitted electrons or in the energy associated with the rupture of a chemical bond (valency electron) we are not in a position to decide. In this connection it is, however, interesting to note that chlorophyll in alcoholic solution shows strong fluorescence of a blood-red colour. The fluorescence appears only in the solution and never in the chloroplasts.

A large amount of experimental work on photo-chemical transformations in carbon compounds has been carried out recently by Professors Ciamician† and Silber at Bologna.

The chemical changes brought about by light in carbon compounds may be assigned to various classes, but the greatest number of such changes may be classed under the heading of the reciprocal oxidation and reduction of two substances, one of which is oxidised at the expense of the other.

One of the most remarkable transformations is the change

* Harvey Gibson, *Annals of Botany*, 22, pp. 117-120, 1908.

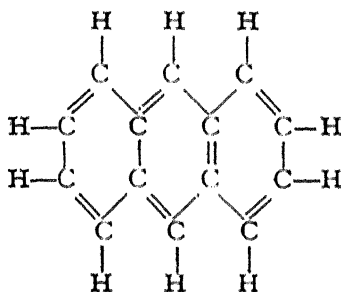
† Ciamician and Silber, "Les Actions chimiques de la Lumière," *Bull. Soc. Chim.*, 6 June, 1908, an address before the Chemical Society of Paris. "The Chemical Action of Light on Organic Compounds," by W. A. Davis. *Science Progress*, 7, 26, pp. 251-279, 1912.

from *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid. The change, unlike most other photo-chemical changes in carbon compounds, takes place very rapidly, being more nearly comparable in this respect with ordinary photographic processes. It is a noteworthy fact that the transformation takes place even in the solid state; in solution it is so rapid that, in a few hours, the tube is full of crystals of the nitroso acid.

The polymerisation of unsaturated compounds under the influence of light attracted attention at an early date. Thus acetylene is transformed into benzene.

A case of particular interest is the change from anthracene * to dianthracene. This change, which is brought about by the action of light, is a reversible one, for in the dark anthracene is reformed. This is said to be the only known instance of a reversible photo-chemical reaction in a homogeneous system. It has been studied by Luther and Weigert,† who find it to obey the law of a unimolecular reaction.

Anthracene ($C_{14}H_{10}$) crystallises in the form of laminæ, or monoclinic plates, which are fluorescent. It melts at $213^{\circ}C.$, and boils above $360^{\circ}C.$ Its chemical structure may be represented as follows :



The change from one stereoisomeric form into another under the influence of light is frequently observed in the case of compounds containing an ethenoid linkage. In many instances ultra-violet rays produce changes which are the converse of those brought about by ordinary light.

* See Chapter VI, p. 82.

† Luther and Weigert, *Zeit. physik. Chem.*, **51**, pp. 297-328, 1904; **53**, pp. 385-427, 1905.

The influence of light on isomeric change has been studied recently by T. M. Lowry and H. R. Courtman.* The solution under examination was protected from purely thermal influences by a water-jacket and exposed to the dazzling radiation of a mercury vapour lamp at a distance of about 5 cm. No acceleration of the isomeric change was observed in the case of the three sugars dextrose, galactose, and maltose, or in the case of nitro-camphor or of hydroxymethylene camphor. In the case of aminomethylene camphor, there is a marked acceleration, which ceases when the stimulus is removed. Benzoyl camphor also undergoes isomeric change more rapidly when exposed to light, but in this case the acceleration persists when the light is extinguished. This is probably due to the liberation of benzoic acid, which acts as a powerful catalyst in promoting isomeric change.

Certain so-called "photo-tropic" substances change in colour when exposed to sunlight, but regain their original colour in darkness. Probably a structural change of a character similar to that of the cases just referred to is here involved. With some substances it is the more refrangible light that brings about the change of colour, while the inverse change is accelerated by the yellow and red rays.

An interesting case of chemical change brought about by light is the transformation of oxygen into ozone by ultra-violet rays. Lenard† has shown that the ozonising action is due to light of extremely short wave-length, less than $200\ \mu\mu$. Regener‡ proved that there is also a deozonising action for wave-lengths between $300\ \mu\mu$ (absorption by glass) and $185\ \mu\mu$ (absorption by quartz). This is in agreement with the fact that ozone shows a strong maximum absorption for light of wave-length $257\ \mu\mu$. Dewar§ has demonstrated the formation of ozone when light falls on liquid oxygen by means of the iodine starch paper test.

Ultra-violet light decomposes water with the formation of hydrogen peroxide, in accordance with the equation

* Lowry and Courtman, *Journ. Chem. Soc.*, 108, pp. 1214-1221, June, 1913.

† Lenard, *Ann. der Physik*, 1, p. 486, 1900.

‡ Regener, *Ann. der Physik*, 20, pp. 1033-1046, 1906.

§ Dewar, *Engineering*, 89, pp. 116-117, 1910.

$2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{H}_2$. This was proved by Kernbaum,* who found a similar effect due to the β -rays of radium. It appears from the experiments of Tian† that light can also bring about the decomposition of hydrogen peroxide in dilute solution, thus: $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$; $2\text{O} = \text{O}_2$. At the end of a sufficient time the gases set free by the action of ultra-violet light upon water are identical with those that would be obtained by electrolysis.

When a solution of rhombic sulphur in carbon bisulphide is exposed to light, amorphous insoluble sulphur is precipitated. In the dark the precipitate redissolves, so that the action is a reversible one.‡ W. D. Bancroft has pointed out that in such reversible photo-chemical processes the phase rule may be applied, regarding light as an additional variable. He finds good agreement between experiment and theory in the case of the precipitation of sulphur.

We may note incidentally an interesting photo-chemical method of detecting ultra-violet rays which has been described by C. Schall.§ A sheet of paper is floated on a solution of 1 part by weight of *p*-phenylene diamine in 14 parts of water and 4 parts of a 40 per cent. solution of nitric acid. The paper is dried by heating and used at once. Diffused daylight only produces a pale-grey tint, but an instant's exposure to the ultra-violet rays from a quartz mercury lamp produces a blue coloration.

THE SO-CALLED "DESTRUCTIVE" ACTION OF RADIATION

Goldstein|| discovered that certain salts, especially the alkaline haloids, become coloured after exposure to kathode rays; at the same time their phosphorescence diminishes. The colours so produced disappear in time, slowly in darkness, when several months may be required, but rapidly in daylight. A rise in temperature hastens this disappearance, for

* Kernbaum, *C. R.*, **148**, pp. 705-706, 1909; **149**, pp. 116-117, 273-275, 1909.

† Tian, *C. R.*, **151**, pp. 1040-1042, 1910; **152**, pp. 1012-1014, p. 1196, 1911.

‡ Rankin, *Journ. Phys. Chem.*, **11**, pp. 1-8, 1907.

§ C. Schall, *Photograph. Wochenblatt*, p. 33, 1907.

|| Goldstein, *Wied. Ann. der Physik*, **54**, p. 371, 1895; **55**, p. 491, 1897.

which a few minutes may then be sufficient. Elster and Geitel* found that the salts thus modified possess considerable photo-electric activity. This property diminishes gradually, and disappears at the same time as the coloration. Certain glasses behave in the same way as these salts, and acquire the photo-electric property under the action of the kathode rays. The coloration produced in salts by the rays from radio-active substances has frequently been noticed. The coloured substances show photo-electric activity.†

In the cases referred to above, light aids in destroying the colour. On the other hand, it has been found that ultra-violet light produces a violet coloration in glasses containing manganese.‡

If, as is probable, the modified substances owe their colour to traces of free metal, it is easy to understand their photo-electric activity. The kathode rays and the ultra-violet light here show a reducing action, while ordinary daylight appears to effect a change of opposite character.

The destruction by one radiation of the chemical effect due to another is a very general occurrence. Thus Wollaston§ found that pale-yellow guaiacum acquires a green colour on exposure to light, but observed that "the two extremities of the spectrum are not only different, but opposite in their chemical effects." Ritter|| of Jena showed that chloride of silver was blackened by ultra-violet rays, and the effect was reversed by the invisible rays beyond the red. Again, the yellow platinocyanide of barium is coloured brown by exposure to Röntgen radiation, but the colour is restored by light, particularly green, yellow, and red light. A photographic dry plate shows a somewhat similar reversal¶ with regard to the action of Röntgen radiation and light.

The destructive action of the red rays of the spectrum on

* Elster and Geitel, *Wied. Ann. der Physik*, **59**, p. 487, 1896.

† Elster and Geitel, *Phys. Zeitschr.*, **4**, pp. 113-114, 1902.

‡ F. Fischer, *Phys. Zeitschr.*, **6**, pp. 216-217, 1905.

§ Wollaston, *Phil. Trans.*, **92**, pp. 365-380, 1802; *Nicholson's Journal*, **8**, pp. 293-297, 1804.

|| Ritter, *Nicholson's Journal*, **8**, pp. 214-216, 1804.

¶ Villard, *Soc. Franc. Phys. Bull.*, pp. 5-27, 1907; *Journal de Physique*, **6**, pp. 369-379, 445-457, 1907.

the photographic image was noticed as long ago as 1843 by J. Herschell. Robert Hunt in his *Researches on Light* (1854) describes the following experiment in illustration of this effect: "By means of two prisms, two spectra are formed, each of which produces upon chloride of silver a chemical change from the green ray to some distance beyond the visible violet. Each spectrum is now so arranged that the inactive yellow and orange rays of the one are thrown upon the most active blue and violet rays of the other. The result is that chemical action is entirely stopped."

This inverse action of the waves of long wave-length has been utilised by Waterhouse for the photography of the infra-red spectrum. The method has been developed by Millochau,* who tints the plates with a colouring medium, such as malachite green, then "solarises" them by exposure to white light, and finally exposes them to the infra-red spectrum. Photographs of the solar spectrum have been obtained from 750 $\mu\mu$ to 950 $\mu\mu$.

It is significant that the red and infra-red rays of the spectrum have the effect of accelerating the exhaustion of a phosphorescing body (Becquerel). We have seen that Lenard explains this by supposing that the long waves shake up the larger systems (S-atoms) to which the separated electrons have become attached, and so make it easier for the electrons to return to the metal atoms. It would appear that a similar explanation might be applied to the inverse action of the long waves in chemical and photographic processes.

THE LATENT IMAGE OF THE PHOTOGRAPHIC PLATE

The nature of the developable image produced on a photographic plate has been the subject of much controversy.† Does a chemical or a physical change take place in the silver salt when a "latent" image is produced? On this question we may quote the words of Chapman Jones.‡

* Millochau, *C. R.*, **142**, pp. 1407-1408, 1906; **143**, pp. 108-110, 1906.

† The views of various investigators have been collected in a series of lengthy papers by W. D. Bancroft in the *Journal of Physical Chemistry*, 1911-1912.

‡ Chapman Jones, *The Science and Practice of Photography*, Chapter XVI.

"A chemical change must be preceded by a physical change; there must be a movement or commotion within the molecule before actual decomposition takes place. The question, therefore, is not whether the change is chemical or physical, but whether it is physical only, or whether it passes beyond the physical stage to an actual decomposition. There certainly is some change, and therefore there is a physical change; but while some consider that this is followed by decomposition, others, including the author, consider that the balance of evidence is overwhelmingly against decomposition."

The experiments of Wiener have shown that the direction of vibration in polarised light which produces photographic action is perpendicular to the plane of polarisation; in other words, it is the electric vector in the light wave which is responsible for the photographic effect. Thus the physical change in the photographic plate is due to the electric vector.

In his interesting presidential address to the Photographic Convention of the United Kingdom Professor J. Joly* puts forward the hypothesis that "the beginnings of photographic action involve an electronic discharge from the light sensitive molecule—in other words, that the latent image is built up of ionised atoms or molecules, upon which the chemical effects of the developer are subsequently directed."

In support of this hypothesis he quotes the experiments of Dewar, who found that the latent image is formed at temperatures approaching the absolute zero.† "This compels us to regard the fundamental effects in the film as other than those of a purely chemical nature. We must seek for the foundations of photographic action in some physical or intra-atomic effect. We must turn for guidance to some purely photo-physical phenomenon. Such an effect is 'photo-electricity.'"

Joly showed that aluminium and silver bromide are photo-electric at about the temperature of liquid air. We have already seen that, apart from secondary effects, photo-electric activity is independent of the temperature.

* Joly, *Nature*, **72**, p. 308, 1905.

† At -180° C. Dewar found 20 per cent., and at -252.5° C. 10 per cent., of the normal photographic effect.

The haloid salts of silver are vigorously photo-electric, and possess an activity in the descending order, bromide, chloride, iodide. This is the order of their photographic sensitiveness. Sensitisers are also photo-electric, their activity being dependent on the absorption of light of some particular colour. An efficient sensitizer must dye the silver halide grain and not merely stain the plate.

We may note also that the photographic image is produced by Röntgen radiation and by Becquerel radiation, which are both known as ionising agents. In this connection it is interesting to remark that the α rays have the same range of action whether tested by the ionisation produced or by their photographic or phosphorescent action.* Experiments carried out by C. G. Barkla prove that the results obtained in the examination of the characteristic "fluorescent" Röntgen radiation of an element are the same whether the ionisation method or the photographic method is employed. The evidence seems conclusive that the photographic process is primarily a result of ionisation.

In their recent work on the theory of the photographic process, Sheppard and Mees† favour the view that the ionisation brings about a chemical change, and the chemical product is the so-called latent image. They think it probable that the half-halide (Ag_2X) is formed and is present in solid solution in the remaining halide. This view is widely accepted at the present time, though it is doubtful whether any direct evidence has been brought forward to prove that halogen is set free in the production of a normal latent image. There are many substances, known to be halogen absorbents, which have no influence in affecting the rate of production of a latent image, though most of them do affect the rate of production of a visible image when it is certain that halogen is being set free.‡

* Rutherford, *Phil. Mag.*, **10**, pp. 163-176, July, 1905; *Radioactivity*, pp. 546-547, 1905.

† Sheppard and Mees, *Investigations on the Theory of the Photographic Process* (Longmans, 1907).

‡ See a discussion in a paper by Sanger Shepherd in the *Photographic Journal*, **35**, pp. 249-257, 1911.

It is fair to claim that the onus of proof lies with those who suggest a chemical change, for there is undoubtedly a physical change taking place, and this physical process is capable, in the light of recent work, of explaining many of the properties of the latent image. There may be outstanding difficulties, such as those connected with the action of oxidising agents, but it is not impossible that these may be satisfactorily explained.

We proceed to an examination of the physical theory of the latent image based on photo-electric action.

Let us suppose that a gel containing grains of silver halide is illuminated by monochromatic light. Then photo-electrons will be liberated from each grain and, in accordance with the results obtained with metal surfaces, the maximum velocity may be taken as dependent on the wave-length of the light, the velocity increasing as the wave-length diminishes. The liberated electrons, after moving for a short time amongst the surrounding molecules, as molecules of air are supposed to move in the interior of a sponge, become attached to neighbouring molecules of the gel. When the illumination ceases a fairly stable arrangement results, consisting of a central grain which is positively charged surrounded by a portion of the gel, roughly spherical in form, in which negative electrons are disseminated. The radius of the sphere will depend upon the velocity of emission—that is, on the wave-length of the exciting light.

The latent image thus formed is not absolutely permanent. The gradual destruction of the image, or “photo-retrogression,” has been studied by Baekeland and others.* According to our view, this is to be explained by the gradual return of electrons to the parent atom, as in Lenard’s theory of phosphorescence. It is significant that Baekeland found photo-retrogression to be very marked in the case of plates, films, or papers kept at a temperature of from 40° to 48° C. for 3 days, while it was not noticeable even after two weeks if the temperature was from 1° to 4° C. This corresponds exactly to the increased rate of decay of phosphorescence due to rise

* Baekeland, *Journ. of Phys. Chem.*, **15**, pp. 314–323, 1911.

of temperature, and may be explained in the same way, as a consequence of the increased rate of vibration of the molecules to which the electrons are attached; for thus the chance of the return of an electron to the silver halide grain is increased.

Objection has been raised to such a physical theory of the latent image on the ground that the assumed stability of the free electric charges remains unexplained. To this we may reply that these charges are located within the substance of the solid. The figures which are usually given for the electrical resistivities of insulators are in many cases nothing more than the resistances of the surfaces. As a parallel case we may draw attention to the phenomena of thermoluminescence.

Another point of significance in connection with this objection is the fact that in the Daguerrotype process the latent image was so evanescent that it was necessary to carry out the development shortly after the exposure.

The view that the processes taking place in the photographic plate are analogous to those postulated by Lenard in connection with phosphorescence is to some extent supported by the fact that the sensitive film fluoresces under the influence of Röntgen rays and radium rays.* In his original communication announcing the discovery of the X-rays, Röntgen says: "It appears questionable, however, whether the chemical action on the silver salts of the photographic plates is directly caused by the X-rays. It is possible that this action proceeds from the fluorescent light which is produced in the glass plate itself, or perhaps in the layer of gelatin. 'Films' can be used just as well as glass plates." Thus it appears that Röntgen suspected fluorescence in the photographic film itself, but his suggestion that the light of fluorescence is sufficient to cause appreciable chemical action is not borne out by some experiments of the writer.† The evidence points rather to the view that the production of luminescence and the formation of the latent image are processes of the same character, each being due to the liberation of photo-electrons by light.

* H. S. Allen, *Proc. Roy. Phil. Soc. Glasgow*, **35**, p. 88, 1903.

† *Proc. Roy. Phil. Soc. Glasgow*, **36**, p. 213, 1905.

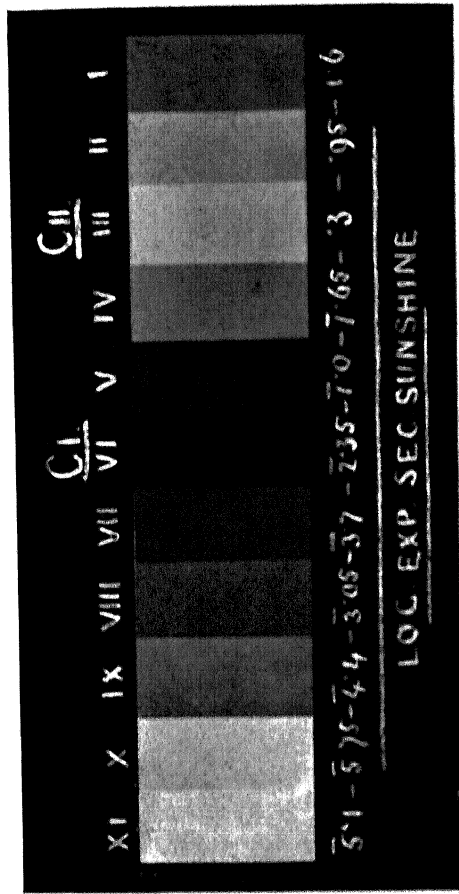


FIG. 35

Reproduction of a paper print by John Sterry, Hon. F.R.P.S., showing the variation of density with increasing exposure. From the least exposure (xi) there is a constant increase in density up to C1 (vi), the first critical point. From C1 to C2 (iii), the second critical point, the density diminishes. This is the period of reversal. From C2 to the greatest exposure (i) is the period of re-reversal.

By permission of the Royal Photographic Society.

PHOTOGRAPHIC REVERSAL

It has been proved experimentally that the mass of silver reduced per unit area of a photographic plate is proportional to the density measured photometrically. A curve may be plotted showing the relation between the density of the developed plate and the time of exposure. The density increases rapidly at first, then more slowly, until it reaches a maximum. This may be called the first critical point. With a longer exposure the density begins to diminish, and reversal of the image sets in. At length a second critical point is reached, where the density has a minimum value corresponding to a destruction of the image. With prolonged exposure the density once more increases and the second reversal of Janssen is obtained.

These variations in density are well illustrated in a reproduction of a print obtained by J. Sterry.*

Photographic reversal has been investigated by R. W. Wood,† who describes four or five different types of such action. The most interesting types from a theoretical standpoint are the ordinary over-exposure reversal, and the reversal due to the action of a second stimulus. In the first case reversal is produced by an exposure three or four hundred times the normal. The effect can be brought about either by ordinary light or by Röntgen rays. In the second case the result produced depends on the order of application of the stimuli. If these are arranged in the following order, pressure marks, Röntgen rays, light shock, and lamplight, the impression due to any one can be reversed by any other which follows it in the list, but in no circumstances by any one preceding it.

Joly has suggested that the phenomena of recurrent reversal may possibly be explained on the view that the latent image is built up of ionised atoms or molecules. The potential between groups of ions may rise until at length a state is attained in which spontaneous neutralisation takes place. He points out that R. W. Wood's results may be capable of explanation on these lines.

* Sterry, *Phot. Journal*, 35, pp. 320-322, 1911.

† R. W. Wood, *Phil. Mag.*, 6, pp. 577-587, 1903.

If we adopt the view already suggested, and trace out an analogy between Lenard's theory of phosphorescence and the formation of a latent image, a certain amount of light may be thrown on these phenomena. We assume that the electrons expelled from the silver halide become attached to molecules of the surrounding dielectric. If these molecules are set in vibration by some external stimulus, such as radiation of long wave-length, the electrons will be enabled to enter again into combination with the atoms from which they were liberated. This recombination is of course effected by the electrostatic forces between the oppositely charged particles. If recombination is not assisted in this way, the electrostatic field will increase under the continued action of light, until, as Joly suggests, spontaneous neutralisation takes place with the destruction of the latent image. The same processes will then recur, giving rise to the second reversal of Janssen.

It would thus appear that there are two processes that may bring about, either independently or in conjunction, the destruction of the latent image—viz. an increase in the motion of vibration of the molecules, and an accumulation of electric charges of opposite sign.

The remarkable phenomena connected with the reversal of the image may perhaps be explained by means of the model suggested above. First we may draw attention to the peculiarities observed when the excitation is due to an intense light lasting for a very short time, or a "light shock." We have seen that the electrons after being liberated remain for some short period in a free state, but finally become attached to the surrounding molecules. In the case of continuous illumination by an ordinary source of light, the electrons first liberated become fixed and will then produce an electric field opposing the emission of later electrons and altering the final arrangement. In the case of a light shock, however, the electrons will be emitted in a rush, and will not have become attached to outside molecules before the emission ceases. Thus we should expect a different final distribution.

R. W. Wood proved that the duration of the light shock to give the Clayden reversal must not exceed $\frac{1}{1000}$ sec., while

the effect could be obtained without difficulty when the exposure was less than $\frac{1}{3000}$ sec. In these experiments an arc lamp was used as the source of light.

When the photographic plate is exposed to a number of stimuli in succession the effect produced depends on the *order* in which the exposures are made. One stimulus differs from another in the velocity with which the electron is ejected from the atom, and perhaps also in the class to which the electron must be assigned. Considering only differences in velocity, let us suppose that two exposures are made, the first causing an emission of electrons with large velocity, the second causing electrons to be set free with smaller velocity. We should then expect the electrons to be arranged, roughly speaking, in concentric spherical shells, somewhat resembling the pleochroic halos in crystals of mica discussed by Professor J. Joly,* and attributed by him to the emission of α particles from a radio-active nucleus. But it must be noticed that the presence of the charges due to the first stimulus sets up an electric field opposing the emission of the slower electrons due to the second stimulus. Consequently the velocity of these will be still further diminished, and they will not be able to travel so far from the parent atoms. Thus the radius of the inner shell will be decreased, and the stage at which spontaneous neutralisation of the charge within this shell takes place will be the more readily reached. The disturbance produced by this neutralisation will be sufficient to upset the equilibrium of the particles at a greater distance from the centre, so that the electrons in the outer shell under the influence of the central attraction will effect their return to the silver halide grain. In this way destruction of the latent image can be brought about.

Let us next consider the case in which the first exposure sets free slowly-moving electrons, while the second causes an emission of electrons with large velocity. These rapidly-moving electrons will have to pass through a shell of attached electrons due to the first exposure, and in consequence their velocity will be somewhat diminished. Thus their final dis-

* Joly, *Phil. Mag.*, 19, pp. 327-330, 1910.

tance from the centre will be smaller than it would have been otherwise, but the position of the inner shell of attached electrons remains unaffected. In consequence, neutralisation would only be brought about after prolonged action of the second stimulus.

To make this clearer, let us imagine that a negative charge A is distributed uniformly over the surface of a sphere of radius a , and that a second charge B is distributed over the surface of a larger sphere of radius b . The corresponding positive charge $A+B$ belongs to the central nucleus. We assume that neutralisation can only take place when the value of the electric intensity becomes great enough to separate one of the electrons from the molecule to which it has become attached. The magnitude of the electric intensity at a point on the inner sphere is $\frac{A+B}{a^2}$, and at a point on the outer sphere is $\frac{B}{b^2}$. The former magnitude is always greater than the latter—that is, neutralisation is always initiated from the inner shell of electrons. Now in the case we are considering a is not affected by the second stimulus, so that we can only bring about neutralisation by giving a large value to B —that is, by prolonged action of the second stimulus producing electrons of high velocity.

In the case previously considered, where the electrons with large velocity are the first to be emitted, a , as we have seen, becomes small, and therefore a small value of A will be sufficient to bring about neutralisation.

This of course is only a crude illustration, as the electrons will be neither arranged symmetrically nor distributed over a spherical surface, but it may serve to show how the resulting effect may be dependent on the order of application of the stimuli.

The order given by R. W. Wood is pressure marks, X-rays, light shock, and lamplight. We have advanced a reason for believing that the electrons emitted under the influence of a light shock will be found at a greater distance from the central grain than those emitted under the influence of lamplight.

We know that the electrons emitted through the incidence of X-rays have greater velocities (between 10^9 and 10^{10} cm. per sec.) than those of the photo-electrons (about 10^8 cm. per sec.). If the proposed theory is correct, the velocity, or at least the displacement, of the electrons due to mechanical pressure must be still greater.

The considerations just advanced suggest that it should be more difficult to produce reversal by the continued action of a single stimulus, when the displacement of the electrons is large than when it is small. The experimental evidence at present available is not sufficient to enable us to decide definitely whether this is so or not, but experiments still in progress lend some support to the suggestion made.

The hypothesis may also help to explain the variations observed in the sensibility of the emulsion with the size of the grain. It is well known that the grain in a rapid plate is considerably larger than the grain in a slow plate; in the process of "ripening" there is a noticeable increase in the size of the halide particles. Apart from the accompanying change in the absorption for light, there will be an effect due to the change in the strength of the electrostatic field which opposes the issue of electrons from the particle. In the case of a grain of radius r from which a number of electrons have escaped, leaving it with a positive charge e , the strength of the field at the surface of the grain will be $\frac{e}{r^2}$. Thus with small grains the field may soon become sufficiently strong to prevent the emission of further electrons, so accounting for the insensitive character of the emulsion, and also for the fact recorded by Lüppo-Cramer* that solarisation occurs less readily the finer the grain, no solarisation at all being found when the grain is extraordinarily fine.

The "reciprocity law" of Bunsen and Roscoe states that provided that It , the product of the light intensity and the time, be constant, the photo-chemical effect of an exposure will be the same whether the intensity or the time be altered. For photographic plates this law fails to hold, and various

* Lüppo-Cramer, *Photographische Probleme*, p. 146, 1907.

modifications * have been proposed. Closely connected with the failure of this law is the fact that a series of intermittent exposures do not yield the same result as a continuous exposure for the same total time. These phenomena receive an explanation by means of the physical theory here suggested. In considering the effect of any given exposure we have to take into account the number of electrons that return to the parent grain. This "fading loss" is probably a most important factor, but we must also consider the effect of attached electrons in retarding the emission of later electrons from the silver halide. It is possible that a quantitative explanation of the observed facts could be developed from this point of view.

The electron theory of the developable image here put forward possesses much greater flexibility than the chemical theory, whose supporters have been compelled to suggest the existence of two or three different latent images or two or three sub-halides in order to account for the complex facts of observation. This complexity has been accentuated by the study of the photographic action of the Röntgen and Becquerel radiations. The physical theory explains these differences by the variations in the velocity and resulting displacement of the electrons; it affords a clue for disentangling the phenomena of reversal, the effect of the size of the grain and of the composition of the emulsion; and finally, it suggests a field for further research in connection with the photo-electric activity of the substances employed, the penetrating power of the electrons, and the dielectric properties of the binding material.

* Sheppard and Mees, *Theory of the Photographic Process*, pp. 214-224; J. Stark, *Ann. d. Physik*, **35**, pp. 461-485, 1911.

INDEX OF AUTHORS

- AIGNER, F., 164, 166
 Aitken, 95
 Allen, H. S., 70, 164-5, 166, 168, 169,
 170-1, 174, 210
 Armstrong, 186
 Arrhenius, 20, 85

 BAKKELAND, 209
 Baeyer, O. v., 38
 — v. and Gehrts, 42, 44
 Baly, 186
 Bancroft, 200, 204, 206
 Bargellini, 182
 Barkla, 9, 84, 208
 Barton, 185
 Becquerel, 69, 77, 85, 183, 184, 195,
 206
 Beil, H., 173
 Bergwitz, 3, 175
 Berndt, 86
 Bichat, 80, 107
 Bloch, E., 68, 80, 89, 91
 Blondlot, 80, 107
 Blythswood, Lord, 78
 Borck. *See* Byk and Borck
 Boyle, 181
 Branly, 4, 108, 124, 160
 Braun, J., 126
 Brewster, David, 181
 Brillouin, 84
 Bronson, 102
 Brown, 200
 Bruninghaus, L., 183
 Buisson, 124, 162-3, 170
 Bunsen, 199, 215
 Byk and Borck, 82

 CANNEGIETER, 92
 Cantor, 83
 Chrisler, 84
 Ciamician, 201
 Compton, 9, 40, 41, 44, 73, 129, 137-
 40, 141, 155-8, 178
 Courtman, H. R., 203
 Crookes, W., 4, 22-4, 49
 Crowther, 173

 DALTON, J. P., 185
 Davis, W. A., 201
 Dawson, H. M., 171
 Dember, H., 3, 5, 6, 73, 101, 115, 175

 Dewar, 183, 197, 203, 207
 Dike, 45

 EBERT, 2, 16
 Eccles, 93
 Einstein, 44, 72, 90, 147, 157, 190-1
 Elster and Geitel, 2, 3, 4, 7, 8, 24, 70,
 74, 78, 97, 101, 111, 116, 119-20,
 122, 124, 126, 141, 160, 174, 205
 Escombe, 200

 FARADAY, 13, 22
 Fischer, F., 205
 Fleming, 21, 70
 Francesconi, 182
 Franck and Hertz, 90

 GEHRTS, 42, 44
 Geissler, 15
 Geitel. *See* Elster and Geitel
 Gibson, Harvey, 201
 Goldmann, 85
 Goldstein, 78, 204
 Griffith, I. O., 112
 Grotthus, 199, 200

 HALLWACHS, W., 2, 3, 16-8, 45, 47,
 49, 69, 70, 73, 80, 85, 91, 107, 109,
 121, 122, 123, 126-7, 141, 159, 161,
 163, 165, 167, 173, 178
 Hänkel, 17
 Harms, 174
 Heaviside, 93
 Helmholtz, 22
 Henry, 94
 Herrmann, 7, 71, 76
 Herschel, John, 181, 206
 Hertz, 1, 13-6, 17, 75, 107, 118, 122,
 146, 159. *See also* Franck and
 Hertz
 Hewitt, 186
 Hodge, 85
 Hoor, 2, 96, 160
 Hughes, A. Ll., 40, 44, 45, 70, 74, 75,
 78-9, 80, 82, 90, 95, 108, 109, 110,
 134-7, 150, 156-7
 Hull, A. W., 132
 Hunt, Robert, 206

 IVES, 196

- JACKSON, H., 183
 Janssen, 211, 212
 Joly, J., 207, 211, 213
 Jones, Chapman, 206-7
- KÄHLER, Karl, 94
 Kauffmann, 186
 Kaye, 23, 24, 89
 Kayser, 181, 185, 186
 Kemp, J. G., 74, 115
 Kernbaum, 204
 Klages, A., 42, 43
 Klatt, 193
 Kleeman, 46
 Knoblauch, O., 75, 81, 83, 100, 167
 Kovarik, 50
 Kowalski, 187
 Kreisler, 61-2, 80, 108, 162, 168
 Küch, R., 100
 Kunz, Jakob, 104, 122, 133
- LABY, 23, 24
 Ladenburg, E., 5, 6, 7, 21, 45, 71, 102-3, 104, 110, 112, 116, 121, 124, 130-3, 141, 174
 — and Markau, 39, 41, 131
 — R., 125
 Larmor, 22
 Le Bon, 5
 Lehmann, 199
 Lenard, P., 4, 5, 6, 7, 11, 24, 30-2, 35-8, 41, 44, 83, 88, 92, 103, 104, 107, 112, 115, 116, 121, 130, 144, 161, 173-4, 178, 183, 192-7, 203, 206, 209, 212
 Lienhop, 6, 41, 100, 104
 Lindemann, R., 3, 10, 107, 149-50, 197
 Lommel, 182, 185
 Lorentz, H. A., 11, 22
 Lowry, T. M., 109, 203
 Luckiesh, 196
 Luggin, 85
 Lüppo-Cramer, 215
 Luther, 199, 202
 Lyman, T., 89, 90, 108, 109, 110
- MARC, 86
 Marconi, 93
 Markau. *See* Ladenburg and Markau
 Martyn, 9
 Maxwell, Clerk, 10, 13, 66, 146
 McClelland, 84
 Mees, 208, 216
 Merritt, 4, 24, 32-4, 182, 186, 192
 Millikan, 108, 134
 — and Winchester, 6, 71-2, 101, 116, 176-7
 Millochau, 206
 Minchin, 69, 85
 Mohlin, 7, 116, 125, 141
 Morton, W. B., 25
 Müller, E., 123
 Murray, Erskine, 73
- NICHOLS, 182, 186, 192
 ONNES, 184, 193
 Owen, G., 94
- PALMER, F., 89, 91
 Partsch, 47, 65-6, 121
 Paterson, 47
 Paul, 191, 196
 Pealing, H., 94
 Planck, 44, 90, 147, 154, 155, 157
 Plogmeier, 81
 Plotnikow, Johannes, 106, 111, 198
 Pochettino, 77, 82, 104, 171
 Pohl, R., 121, 122, 129, 141, 196-7
 — and Pringsheim, 8, 9, 84, 127-9, 141, 143, 150
 Ponsen, 52
 Pringsheim. *See* Pohl and Pringsheim
- RAMSAUER, 92, 93, 95
 Ramsay and Spencer, 71, 76, 77, 161, 171
 Rankin, 204
 Rayleigh, Lord, 185
 Raymond, 3
 Regener, 203
 Reiger, R., 82-3
 Retschinsky, T., 109
 Richardson, 9, 40, 44, 73, 120, 137-40, 141, 153-8
 Richtmyer, 7, 113
 Riecke, 45
 Ries, 86
 Right, 2, 18-20, 24, 97, 107
 Ritter, 205
 Robinson, J., 45, 46-7, 121, 177-8
 Rohde, 76, 81
 Röntgen, 210
 Roscoe, 199, 215
 Rubens and Ladenburg, 45
 Rudolph, W., 124
 Rutherford, 49, 143
- SADZEWICZ, 169
 Saeland, 11, 192
 Schall, C., 204
 Schmidt, G. C., 75, 80, 185-6, 190, 197
 Scholl, 85
 Schumann, 89, 108, 109
 Schweidler, E. v., 53, 56, 163, 169, 170, 174
 Seoble, W. A., 107
 Sheppard, 208, 216
 Silber, 201
 Soddy, F., 120
 Spencer. *See* Ramsay and Spencer
 Spiers, F. S., 176
 Spring, W., 182
 Stark, 81, 89, 94, 109, 143, 188-92, 199, 216

- Stark and Steubing, 81, 82, 190
Sterry, J., 211
Steubing, 94, 184. *See also* Stark and Steubing
Stevenson, L. S., 82
Stewart, 4, 24, 32-4
Stokes, G. G., 29, 181-2, 184
Stoletow, 2, 18, 20, 53-6, 64, 80, 97, 160
Stoney, Johnstone, 22
Stuhlmann, 46

THOMSON, J. J., 4, 11, 23-30, 49, 53, 83, 88, 89, 97, 123, 143, 146, 150-53, 187, 188
Tian, 204
Townsend, 50, 63-4, 66
Tyndall, 95

ULLMANN, E., 69, 73, 164, 166, 167, 168, 169
Unwin, 6, 98-100

VARLEY, W. M., 6, 57-61, 98-100, 107, 111, 167

Varley, 22
Villard, 205
Voigt, 186

WATERHOUSE, 206
Wehnelt, 89
Weigert, 202
Werner, 195
Whiddington, 94
Wiedemann, 2, 16, 180, 185-6, 197
Wien, 147, 154
Wiener, 207
Wildermann, 85, 199
Wilson, C. T. R., 28, 90, 95
— W., 78, 79, 83, 86
Winchester. *See* Millikan and Winchester
Wollaston, 205
Wood, R. W., 110, 183, 211, 212, 214
Wright, J. R., 7, 116, 134
Wulf, T., 67, 168

ZEEMAN, 22, 142
Zeleny, 97-8

INDEX OF SUBJECTS

- ABSORPTION of light, 15, 81, 89-92,
 123, 152, 182, 191
 Actino-electricity, 1
 Air, photo-electric activity of, 88,
 89, 90, 91
 Aniline dyes, 80-81
 Anthracene, 82, 94, 171, 202
 Atmospheric ionisation, 93-4
 Atom, 10, 22, 143

 BATTERY, photo-electric, 19-21
 Becquerel effect, 77, 85
 — radiation, 84, 180, 208, 210, 213

 CANAL rays, 5, 180, 188
 Carbon dioxide, photo-electric acti-
 vity of, 88, 89, 90
 — — current in, 61, 64, 65
 Charge of an electron, 23
 Chlorophyll, 200-201
 Chromophores, 182, 190
 Condensation nuclei, 28, 92, 93, 95
 Conductivity, electrical. *See* Resist-
 ance
 Contact difference of potential, 17,
 19, 21, 41, 169, 178
 Critical pressure, 55, 64
 Cycloidal path of electron, 26

 DESTRUCTIVE action of radiation,
 204-206
 Developable image, 206-210
 Direction of emission of photo-elec-
 trons, 44-5

 ELECTRIC field and current strength,
 52 *et seq.*
 Electromagnetic waves, 1, 13, 93-4
 Electron, 22-34
 Emergent effect, 45-8

 FATIGUE, photo-electric, 3, 159-179
 Films, thin metallic, 45-8
 Fluor-spar, 78
 Fluorescence, 82, 180-197, 210

 GASES, photo-electric activity of,
 88-95
 — — current in, 49-67

 HALIDES, metallic, 77-9, 85-6, 207-
 208

 Helium, 3, 64, 74
 Hydrogen, photo-electric activity of,
 88, 89, 91
 — — current in, 61, 64, 65, 67,
 74, 167-8, 174
 — peroxide, 172, 203

 INCIDENT and emergent effect, 45-8
 Insulators, photo-electric activity of,
 82-3
 Intensity of light, influence of, on
 photo-electric phenomena, 6-7,
 111-7
 Ionisation by collision, 4, 50-1, 63-7
 — and luminosity, 187
 Ions in gases, 49-50, 51-4, 63-7,
 88-95
 Isomeric changes, 202-3

 KATHODE rays, 4, 22-4, 32, 34, 180,
 204

 LATENT image, 11, 206-210
 Luminescence. *See* fluorescence and
 phosphorescence

 MAGNETIC field, effect of, on current,
 4
 — — on path of electron, 24-6,
 32-4, 40
 Mercury vapour lamp, 108-9
 Metallic compounds, photo-electric
 activity of, 75-9
 Metals, photo-electric activity of,
 69-75
 Mono-chromatic light, 110-111

 NITROGEN, photo-electric activity
 of, 91
 " Normal " effect, 7, 8, 9, 11, 118,
 128-9
 Number of electrons, 5, 6, 104, 111-5,
 122-9, 141, 154-8

 ORGANIC compounds, photo-electric
 activity of, 80-83
 Oxygen, action of light on, 203
 — photo-electric activity of, 88, 91,
 137
 — — current in, 65, 67
 Ozone, 67, 164, 167, 168, 203

- PENETRATION of ultra-violet light, 121
- Phosphorescence, 11, 23, 75, 104, 180-197, 210
- Photo-chemistry, 11, 95, 198-206
- Photography, 11, 206-216
- Photokatalytic reactions, 198
- Photometry, 3, 111-5, 163, 166
- Photo-retrogression, 209
- Photo-tropism, 203
- Polarisation of light, influence of, 7, 8, 118-122, 127-8
- Polymerisation, 202
- Positive electricity, discharge of, 4-5
- Potassium cell, construction of, 3, 74
- Pressure of gas, influence of, on photo-electric current, 49-65, 175-9
- QUANTUM theory of radiation. *See* unitary theory
- RADIATION, 143, 150-153. *See* unitary theory
- Reciprocity law, 215
- Recovery of photo-electric activity, 163-5
- Reflection of electrons, 38-40, 42-3
- Resistance, change of, on illumination, 1, 85-7
- Resonance, 148-150, 185
- Reversal, 206, 211-5
- Röntgen radiation, 9, 84, 145, 180, 208, 210, 211
- "SELECTIVE" effect, 7, 8, 9, 11, 118, 128-9, 143, 149-150, 196
- Sensitiveness of photo-electric cell, 74
- Sodium cell, construction of, 74
- Sodium-potassium alloy, construction of cell containing, 21
- Solarisation. *See* reversal
- Solid solutions, 183, 208
- Sources of light, 16, 106-111
- Sparking potential, 1, 13-16, 50, 61-3, 66
- Sulphides, metallic, 75-7
- Sulphur, 204
- Surface films, 67, 81, 172-3, 179
- TELEGRAPHY, wireless. *See* electromagnetic waves
- Temperature, influence of, 6, 96-105, 183, 193, 207
- Thermo-luminescence, 197, 210
- UNITARY theory of radiation, 10, 44, 146-8, 151-3, 155, 157, 190
- VALENCY electrons, 11, 143, 180, 188-189, 198
- Vapours, photo-electric activity of, 94-5
- Velocity distribution curves, 6, 35-44, 101, 131
- of electrons, 5, 6, 35-48, 101, 103, 104, 115-7, 130-141, 154-8
- WAVE-LENGTH, influence of, 8-9, 122-140

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